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(54) **CONDUCTIVE MATERIAL DISPERSION, METHOD FOR PRODUCING SAME, COMPOSITION FOR SECONDARY BATTERY ELECTRODES USING SAME, ELECTRODE MEMBRANE, SECONDARY BATTERY AND VEHICLE**

(57) Provided is a conductive material dispersion including: a conductive material containing at least one kind selected from the group consisting of a carbon nanotube and carbon black; carboxymethyl cellulose or its salt; and water. The carboxymethyl cellulose or its salt

has a weight average molecular weight of 10,000 to 150,000 and an etherification degree of 0.5 to 0.9. A product of the complex elastic modulus (Pa) and the phase angle (°) of the conductive material dispersion is 100 or more and 1,500 or less.

Description**TECHNICAL FIELD**

5 [0001] The present invention relates to a conductive material dispersion, a method for producing the same, and a composition for a secondary battery electrode, an electrode film, a secondary battery, and a vehicle using the conductive material dispersion.

BACKGROUND OF THE INVENTION

10 [0002] The capacity of lithium ion secondary batteries greatly depends on the positive electrode active material and the negative electrode active material as the main material. Therefore, various materials have been studied actively. However, the charging capacity of all the active materials in practical use has reached close to the theoretical value and improvements are close to the limit. If the amount of the active material filled in the battery is increased, the capacity 15 can be simply increased. Therefore, an attempt has been made to reduce the addition amounts of a conductive material and binder which do not directly contribute to the capacity. Between them, the conductive material forms a conductive path inside the battery and has a role of preventing cutting of the conductive path due to the expansion and contraction of the active material by connecting the active material particles. It is effective to form an efficient conductive network by using a conductive material dispersion in order to maintain the performance with a small addition amount (Patent 20 Literature 1).

[0003] As conductive materials, carbon black, Ketjen black, graphene, fine carbon materials, and the like are used. Suppose that a carbon nanotube having a small outer diameter and a large specific surface area in particular is used among carbon nanotubes which are a kind of fine carbon fibers. In the above case, it is possible to efficiently form a conductive network with a small amount and reduce the amount of conductive material contained in a positive electrode 25 and a negative electrode of a lithium ion secondary battery. By adding carbon nanotubes to a graphite or silicon negative electrode, the electrode resistance is reduced, the load resistance of the battery is improved, the strength of the electrode is increased, and the expansion/contraction property of the electrode is increased. Accordingly, the cycle life of a lithium ion secondary battery is improved (Patent Literatures 2, 3 and 4). Silicon-based active materials have higher theoretical 30 capacity than graphite and can contribute to higher battery capacity. However, the volume change associated with charge and discharge is remarkable. Therefore, an attempt has been made to pulverize a silicon-based active material, form a thin carbon film on the surface of the particles, and use it in combination with graphite in order to improve the cycle life.

[0004] In a negative electrode in which graphite and a silicon-based active material are used in combination, the selection of a binding agent becomes a very difficult problem. The styrene-butadiene rubber (SBR) used in the graphite single system has remarkably deteriorated characteristics in the system in which graphite and a silicon-based active 35 material are combined. The SBR is designed to bind active material particles with particles of rubber and to bring the active material into contact with an electrolyte. However, if a silicon-based negative electrode active material of which the expansion and contraction is larger than that of graphite is contained, the SBR alone has a weak binding force and there is a problem that the binding is broken at the beginning of the charge/discharge cycle. Therefore, a method has 40 been employed in which an SBR is used with a binding agent such as polyacrylic acid or polyacrylic acid salt uniformly dispersed or dissolved in water, and accordingly the surface of the active material is widely covered with the binding agent and the surface resin layer binds the active material together (Patent Literature 5). However, when a low molecular weight polyacrylic acid or polyacrylic acid salt is used as a binder, good cycle characteristics cannot be obtained (Patent Literature 6 and Non-Patent Literature 1).

[0005] With regard to the positive electrode also, studies have been performed to reduce the electrode resistance by 45 adding carbon nanotubes (Patent Literatures 7 and 8). Many of the positive electrode active materials are unstable with respect to water, but lithium iron phosphate is relatively stable with respect to water, for example. From the above, a secondary battery electrode can be produced by using water as a dispersion medium. Since lithium iron phosphate is particularly poor in conductivity, it is common to use it by forming a thin carbon film. Since lithium iron phosphate has a high lithium diffusion resistance in a solid, a method for improving the resistance as an electrode film by using it as fine 50 particles is known.

[0006] In addition, from the viewpoint of environmental load reduction and cost reduction, the demand for a conductive material dispersion using water as a dispersion medium is increasing. However, carbon nanotubes are difficult to disperse 55 into water because carbon nanotubes have high hydrophobicity and various attempts have been reported. Patent Literature 9 discloses a dispersion of a carbon nanotube-containing composition containing carboxymethyl cellulose or its salt having a weight average molecular weight of 5000 or more and 60,000 or less which is measured based on gel permeation chromatography and an aqueous solvent, for example. Patent Literature 10 discloses a dispersion of a carbon nanotube-containing composition containing a dispersion medium and a dispersing agent containing carboxymethyl cellulose or its salt having an etherification degree of 0.4 or more and less than 0.7. Patent Literature 11 discloses

a method for improving conductivity by dispersing, in water, a carbon nanotube having an outer diameter of 50 nm or more and 110 nm or less together with carboxymethyl cellulose sodium salt and using the carbon nanotube for a secondary battery electrode.

[0007] Patent Literature 12 discloses a conductive material dispersion using carboxymethyl cellulose having an average polymerization degree of 500 or more and 2500 or less. In order to obtain a viscosity suitable for coating, the dispersion is performed by using a bead mill and there was a problem that the structure of the conductive material is reduced. Patent Literature 13 discloses a conductive material dispersion containing carbon black having a specific surface area of 25 m²/g or more and 300 m²/g or less. A large amount of dispersing agent was required to prepare a conductive material dispersion with excellent dispersion stability. Patent Literature 14 discloses an aqueous conductive material dispersion using ethyl cellulose as a dispersing agent. However, it was difficult to include a high concentration of the conductive material in the dispersion to prepare a conductive material dispersion excellent in dispersibility.

[0008] In general, the smaller the outer diameter of the carbon nanotube, the larger the specific surface area. Therefore, the wettability with respect to water deteriorates and it becomes difficult to obtain a highly concentrated and good dispersion. However, carbon nanotubes having a smaller outer diameter and a higher specific surface area can ideally form an efficient conductive network. Therefore, it has been an urgent matter to obtain a dispersion in which carbon nanotubes having a small outer diameter and a high specific surface area are well dispersed. Further, in a dispersion having a low concentration of carbon nanotubes, there arises a problem that the degree of design freedom is reduced when a material such as an active material or a binder is mixed therein, and a problem that the transportation cost per carbon nanotube solid content is increased. Therefore, it has also been required to disperse carbon black or carbon nanotubes having a small outer diameter and a high specific surface area at a high concentration.

Citation List

Patent Literature

[0009]

Patent Literature 1: Japanese Patent Application Publication No. 2005-162877

Patent Literature 2: Japanese Patent Application Publication No. Hei 4-155776

Patent Literature 3: Japanese Patent Application Publication No. Hei 4-237971

Patent Literature 4: Japanese Patent Application Publication No. 2004-178922

Patent Literature 5: Japanese Patent Application Publication No. 2013-229163

Patent Literature 6: U.S. Patent No. 8034485

Patent Literature 7: Japanese Patent Application Publication No. 2011-70908

Patent Literature 8: Japanese Patent Application Publication No. 2005-162877

Patent Literature 9: Japanese Patent Application Publication No. 2014-002885

Patent Literature 10: Japanese Patent Application Publication No. 2016-204203

Patent Literature 11: Japanese Patent Application Publication No. 2016-028109

Patent Literature 12: Japanese Patent Application Publication No. 2017-10822

Patent Literature 13: Japanese Patent Application Publication No. 2017-84682

Patent Literature 14: Japanese Patent Application Publication No. 2011-70908

Non-Patent Literature

[0010] Non-Patent Literature 1: J. Electrochem. Soc. 2008, 155, A812-A816

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

5 [0011] The dispersions of the carbon nanotube-containing compositions disclosed in Patent Literatures 9 and 10 are not able to contain carbon nanotubes of several mass% or more, for example. Further, the dispersion disclosed in Patent Literature 11 does not have sufficient dispersibility for dispersing carbon nanotubes having a small outer diameter and a high specific surface area. Further, since a carbon nanotube dispersion at a high concentration tends to generate aggregates and precipitates during storage, the dispersion also has a problem in terms of storage stability. In order to prevent sedimentation, a method is effective in which the viscosity of the carbon nanotube dispersion is increased by using a dispersing agent having a high molecular weight. However, there are also problems in which the coating property is lowered and gelation easily occurs. Further, in the method for preparing a negative electrode for a secondary battery disclosed in Patent Literature 5, the following are recommended: a method of adding dissolved polyacrylic acid to a composition for a secondary battery electrode and performing a coating treatment on the surface of a silicon-based active material. However, if carbon nanotubes are used as conductive materials, there has been a problem that a nonuniform distribution of polyacrylic acid occurs even if the above method is used.

10 [0012] Further, the inventors have found, as a result of studies, that it is difficult to obtain a high concentration and good dispersion state using water as a dispersion medium, for an active material such as a silicon-based active material or lithium iron phosphate which is pulverized and has a carbon film formed on the surface thereof for the same reason as the above carbon nanotubes. Therefore, it has been found that it is particularly difficult to obtain a good dispersion state when an active material such as a silicon-based active material or lithium iron phosphate which is pulverized and has a carbon film formed on the surface thereof is combined with carbon nanotubes in addition to various active materials. As a result, it is found that it is also difficult to obtain a secondary battery having excellent rate characteristics and cycle characteristics.

15 [0013] An object of the present invention is to provide a conductive material dispersion having high concentration and high dispersibility and a composition for a secondary battery electrode in order to obtain an electrode film having high conductivity. More specifically, an object of the present invention is to provide a secondary battery having excellent rate characteristics and cycle characteristics.

20 [0014] An object of an embodiment of the present invention is to provide a conductive material dispersion having a high concentration and high dispersibility and a method for producing the same. Another object of another embodiment of the present invention is to provide a composition for a secondary battery electrode. Still another object of a still another embodiment of the present invention is to provide an electrode film capable of enhancing the output and cycle life of a secondary battery and a secondary battery having a high output and a good cycle life. Still yet another object of still yet another embodiment of the present invention is to provide a vehicle including a secondary battery.

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MEANS FOR SOLVING THE PROBLEM

30 [0015] As a result of intensive studies made by the present inventors, a conductive material dispersion contains carboxymethyl cellulose or its salt having a specific weight average molecular weight and an etherification degree and a conductive material containing at least one kind selected from the group consisting of a carbon nanotube and carbon black. The carbon nanotube and/or carbon black can be satisfactorily dispersed in water and a good conductive network can be maintained with a small addition amount by performing dispersing such that the product (X × Y) of the complex elastic modulus X (Pa) and the phase angle Y (°) becomes 100 or more and 1,500 or less. This can enhance the rate characteristic and the cycle life of a secondary battery.

35 [0016] Examples of embodiments of the present invention are shown below.

40 [0017] An embodiment of the present invention relates to a conductive material dispersion including: a conductive material containing at least one kind selected from the group consisting of a carbon nanotube and carbon black; carboxymethyl cellulose or its salt; and water, in which the carboxymethyl cellulose or its salt has a weight average molecular weight of 10,000 to 150,000 and an etherification degree of 0.5 to 0.9, and a product (X × Y) of a complex elastic modulus X (Pa) and a phase angle Y (°) of the conductive material dispersion is 100 or more and 1,500 or less.

45 [0018] Another embodiment of the present invention relates to the conductive material dispersion in which the carboxymethyl cellulose or its salt has a weight average molecular weight of 10,000 to 100,000.

50 [0019] Another embodiment of the present invention relates to a conductive material dispersion including: a carbon nanotube; carboxymethyl cellulose or its salt; and water, in which the carboxymethyl cellulose or its salt has a weight average molecular weight of 10,000 to 100,000 and an etherification degree of 0.5 to 0.9, and a product (X × Y) of a complex elastic modulus X (Pa) and a phase angle Y (°) of the conductive material dispersion is 100 or more and 1,500 or less.

55 [0020] Another embodiment of the present invention relates to the conductive material dispersion in which the amount

of acidic group of the carbon nanotube is 0.1 to 0.8 $\mu\text{mol}/\text{m}^2$.

[0021] Another embodiment of the present invention relates to the conductive material dispersion in which the amount of acidic group of the carbon nanotube is 40 to 500 $\mu\text{mol}/\text{g}$.

5 [0022] Another embodiment of the present invention relates to the conductive material dispersion in which the complex elastic modulus is 50 Pa or less and the phase angle is 15 degrees or more.

[0023] Another embodiment of the present invention relates to the conductive material dispersion in which the carbon nanotubes includes a first carbon nanotube having an average outer diameter of 0.5 nm or more and less than 5 nm and a second carbon nanotube having an average outer diameter of 5 nm or more and 20 nm or less, and a mass ratio of the first carbon nanotube to the second carbon nanotube is 1:10 to 1:100.

10 [0024] Another embodiment of the present invention further relates to the conductive material dispersion further including a polyacrylic acid.

[0025] Another embodiment of the present invention relates to the conductive material dispersion in which a median diameter of the conductive material dispersion is 0.5 μm or more and 2.0 μm or less.

15 [0026] Another embodiment of the present invention relates to the conductive material dispersion in which the conductive material dispersion has a TI value of 2.0 to 5.0.

[0027] Another embodiment of the present invention relates to the conductive material dispersion in which a gloss of a coating film of the conductive material dispersion measured at 60 degrees relative to an incident angle is 5 to 120.

20 [0028] Another embodiment of the present invention relates to the conductive material dispersion in which pH of the conductive material dispersion is 7.0 to 10.5.

[0029] Another embodiment of the present invention relates to a composition for a secondary battery electrode including the conductive material dispersion described above.

[0030] Another embodiment of the present invention relates to an electrode film including a coating film of the composition for a secondary battery electrode described above.

25 [0031] Another embodiment of the present invention relates to a secondary battery including the electrode film described above.

[0032] Another embodiment of the present invention relates to a method for producing the conductive material dispersion described above in which steps of (1) and (2) below are performed in this order, the method including: (1) a step of performing dispersing at a pressure of 60 to 120 MPa by using a high-pressure homogenizer and setting a median diameter to 4.0 μm or less; and (2) a step of performing dispersing until a phase angle becomes 40 degrees or more by using a bead mill.

30 [0033] Another embodiment of the present invention relates to a vehicle including the secondary battery described above.

ADVANTAGEOUS EFFECT OF THE INVENTION

35 [0034] According to embodiments of the present invention, it is possible to provide a conductive material dispersion having a high concentration and high dispersibility and a method for producing the same, and a composition for a secondary battery electrode. Further, according to embodiments of the present invention, it is possible to provide an electrode film capable of enhancing the output and cycle life of a secondary battery and a secondary battery having a high output and a good cycle life. According to embodiments of the present invention, it is possible to provide a vehicle including a secondary battery.

DETAILED DESCRIPTION OF THE INVENTION

45 [0035] Hereinafter, a carbon nanotube, carbon black, carboxymethyl cellulose and its salt, carbon nanotube and carbon black dispersions, a composition for a secondary battery electrode, an electrode film, a secondary battery, a vehicle, and the like of embodiments of the present invention will be described in detail. The present invention is not limited to the following embodiments, and the present invention also includes embodiments that are implemented without changing the gist of the present invention.

50 [0036] A carbon nanotube is sometimes referred to herein as "CNT". Carboxymethyl cellulose is sometimes referred to as "CMC". In the present specification, the conductive material dispersion may be simply referred to as a "dispersion".

<Conductive material dispersion>

55 [0037] The conductive material dispersion contains at least one kind selected from the group consisting of CNT and carbon black as conductive materials, CMC or its salt, and water.

[Carbon nanotube]

[0038] A carbon nanotube (CNT) that can be used as a conductive material has a shape in which planar graphite is cylindrically wound. The carbon nanotube includes a single-walled CNT or a multi-walled CNT and may include a combination thereof. The single-walled CNT has a structure in which one layer of graphite is wound. The multi-walled CNT has a structure in which two or three or more layers of graphite are wound. In addition, the sidewalls of the CNT do not need to have a graphite structure. It is assumed that a CNT that has sidewalls having an amorphous structure is also included in the CNT of the present specification, for example.

[0039] The shape of the CNT is not limited. Examples of the shape of the CNT include a variety of shapes such as a needle-like shape, a cylindrical tube-like shape, a fishbone-like shape (fishbone or cup-stacked type), a playing card-like shape (platelet), and a coil-like shape. In the present embodiment, the CNT preferably has a needle-like shape or a cylindrical tube-like shape from among the above. The CNT may have a single shape or a combination of two or more shapes.

[0040] Forms of the CNT include a graphite whisker, filamentous carbon, a graphite fiber, an ultrafine carbon tube, a carbon tube, a carbon fibril, a carbon microtube, and a carbon nanofiber, for example. The CNT may have a single form from among the above or a combination of two or more forms.

[0041] The amount of an acidic group of the CNT can be determined from the adsorbed amount of hexylamine based on back titration. The amount of acidic group of the CNT determined from the adsorbed amount of hexylamine is preferably 0.1 $\mu\text{mol}/\text{m}^2$ or more and more preferably 0.2 $\mu\text{mol}/\text{m}^2$ or more based on the surface area of the CNT calculated based on the BET method. Further, the amount of acidic group is preferably 0.8 $\mu\text{mol}/\text{m}^2$ or less and more preferably 0.7 $\mu\text{mol}/\text{m}^2$ or less. The amount of acidic group of the CNT determined from the adsorbed amount of hexylamine is preferably 40 $\mu\text{mol}/\text{g}$ or more, more preferably 50 $\mu\text{mol}/\text{g}$ or more, and still more preferably 120 $\mu\text{mol}/\text{g}$ or more based on the mass of the CNT. Further, the amount of acidic group is preferably 500 $\mu\text{mol}/\text{g}$ or less, more preferably 250 $\mu\text{mol}/\text{g}$ or less, and still more preferably 220 $\mu\text{mol}/\text{g}$ or less. By setting the amount of acidic group of the CNT in the above range, the affinity balance between the CMC and water as the dispersion medium is improved, and accordingly an excellent conductive material dispersion can be obtained. A conductive material dispersion containing CNT is also referred to as a CNT dispersion.

[0042] The outer diameter of the CNT is preferably 0.5 nm or more, more preferably 1 nm or more, and still more preferably 5 nm or more. Further, the outer diameter is preferably 30 nm or less, more preferably 20 nm or less, and still more preferably 13 nm or less. The average outer diameter is obtained by first observing and capturing an image of the CNT by using a transmission electron microscope. Next, any 300 CNTs in the observation photograph are selected and the outer diameter of each CNT is measured. Accordingly, the average outer diameter can be calculated by using the average value.

[0043] Suppose that two or more kinds of CNTs having different average outer diameters are used as the CNT. In the above case, the average outer diameter of a first CNT is preferably 0.5 nm or more and more preferably 1 nm or more. The average outer diameter is preferably less than 5 nm. The average outer diameter of a second CNT is preferably 5 nm or more and 30 nm or less and more preferably 5 nm or more and 20 nm or less. The average outer diameter of the CNT can be calculated by observing the forms of the CNT by using a transmission electron microscope (manufactured by JEOL) and measuring the lengths of the short axes and using the number and the average value.

[0044] Suppose that two or more kinds of CNTs having different average outer diameters are used as the CNT. In the above case, the mass ratio of the first CNT to the second CNT is preferably 1:10 to 1:100 and more preferably 1:10 to 1:50.

[0045] A CNT having a small outer diameter is preferable because the CNT can conduct between active materials in an electrode layer which are separated by a distance and easily follows the expansion and contraction of the active materials in accordance with charging and discharging. In addition, a CNT having a large outer diameter is preferable because the CNT can conduct between active materials which are close to each other and has a high probability of contact with the active materials.

[0046] The specific surface area of the CNT is preferably 100 m^2/g or more, more preferably 150 m^2/g or more, and still more preferably 200 m^2/g or more. Further, the specific surface area is preferably 1200 m^2/g or less and more preferably 1000 m^2/g or less. The specific surface area of the CNT is calculated based on the BET method by means of nitrogen adsorption measurement.

[0047] The carbon purity of the CNT is expressed by the content (mass%) of carbon atoms in the CNT. The carbon purity is preferably 80 mass% or more, more preferably 90 mass% or more, still more preferably 95 mass% or more, and particularly preferably 98 mass% or more relative to 100 mass% of the CNT. By setting the carbon purity to the above range, it is possible to prevent a defect such as the occurrence of a short caused by the formation of dendrite due to an impurity.

[0048] The content of the CNT is preferably 0.2 mass% or more, more preferably 0.4 mass% or more, and still more preferably 1 mass% or more of the non-volatile content of the conductive material dispersion. Further, the content of the CNT is preferably 30 mass% or less, more preferably 20 mass% or less, and still more preferably 10 mass% or less.

By making the content of the CNT into the above range, the CNT can be favorably and stably present without causing sedimentation and gelation. It is preferable that the content of the CNT is adjusted appropriately such that a carbon nanotube dispersion having an appropriate fluidity or viscosity can be obtained by means of the specific surface area of the CNT, the affinity to the dispersion medium, the dispersing ability of the dispersing agent, and the like.

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[Carbon black]

[0049] Examples of the carbon black include acetylene black, furnace black, hollow carbon black, channel black, thermal black, Ketjen black, and the like. The carbon black may be neutral, acidic, or basic. Carbon black subjected to an oxidation treatment or carbon black subjected to a graphitization treatment may be used.

[0050] The average primary particle diameter of the carbon black is preferably 0.01 to 1 μm , more preferably 0.01 to 0.2 μm , and still more preferably 0.01 to 0.1 μm as similar to the average primary particle diameter range of carbon black used in general dispersions or paints. The average primary particle diameter here refers to an arithmetic mean particle diameter measured by using an electron microscope. This physical property value is generally used to represent physical properties of carbon black.

[0051] The BET specific surface area and pH are known as other physical property values representing the physical properties of carbon black. The BET specific surface area refers to the specific surface area (hereinafter referred to simply as specific surface area) measured based on the BET method by means of nitrogen adsorption. The specific surface area corresponds to the surface area of carbon black. The larger the specific surface area, the larger the amount of dispersing agent required. The pH changes by being affected by functional groups and contained impurities of the surface of carbon black.

[0052] The BET specific surface area of carbon black is preferably 20 to 1500 m^2/g , more preferably 30 to 1000 m^2/g , and particularly preferably 100 to 300 m^2/g .

25 [Carboxymethyl cellulose or its salt]

[0053] The carboxymethyl cellulose (CMC) or its salt is an anionic water-soluble polymer which is obtained by using cellulose as a raw material. The weight average molecular weight of the CMC is preferably 10,000 or more. Further, the weight average molecular weight is preferably 150,000 or less, more preferably 100,000 or less, and still more preferably 70,000 or less. The weight average molecular weight is more preferably 60,000 or less and particularly preferably 30,000 or less. By setting the weight average molecular weight in the above range, the intermolecular forces of the CMC, and the CNT and carbon black, and the intermolecular forces of the CMC and water are well balanced, and the CMC can be satisfactorily dispersed and maintained in a state. The etherification degree of the CMC is preferably 0.5 or more and more preferably 0.6 or more. Further, the etherification degree is preferably 0.9 or less and more preferably 0.8 or less. By setting the etherification degree in the above range, the CMC can have an appropriate affinity with water, CNT and carbon black. Further, if a secondary battery is used, it is possible to prevent a defect in which the dispersing agent is dissolved in the electrolyte in the battery and the viscosity of the electrolyte increases.

[0054] The method for producing the CMC or its salt is not particularly limited, and the CMC or its salt can be produced by means of a general method for producing CMC or its salt. The CMC or its salt is produced by performing a mercerization reaction in which an alkali is reacted with cellulose, and then adding an etherifying agent to the obtained alkali cellulose to perform an etherification reaction. The CMC or its salt can be produced as follows, for example: after a mercerization reaction is performed by using a mixed solvent containing water and an organic solvent, an etherification reaction is performed by adding monochloroacetic acid, and after the excess alkali is neutralized with an acid, the mixed solvent is removed, washed, dried, and then pulverized. The cellulose raw material can be reduced in molecular weight by extending the reaction time of the mercerization reaction.

[0055] The weight average molecular weight of the CMC is preferably 10,000 or more and more preferably 15,000 or more based on the weight average molecular weight of pullulan. Further, the weight average molecular weight is preferably 100,000 or less, more preferably 60,000 or less, and still more preferably 30,000 or less. If the CMC has an appropriate weight average molecular weight, the adsorbability to the CNT and carbon black is enhanced, and the stability of a dispersion element is further enhanced. In addition, by setting the weight average molecular weight in the above range, the hygroscopicity becomes high, and the deterioration in the film strength can be suppressed. Further, it is possible to prevent an increase in the viscosity due to hydrogen bonding in the aqueous solution and deterioration in the charging property and the machine storage stability of the CNT and carbon black. In addition, suppose that the dispersing machine used is a type in which a liquid to be dispersed passes through a narrow channel such as a nozzle type high-pressure homogenizer. In the above case, transfer to the narrow channel becomes difficult, and deterioration in the dispersion efficiency can be suppressed.

[0056] There are many commercially available CMCs having a higher molecular weight than the above preferred range. Therefore, the CMCs may be reduced in molecular weight by being subjected to a hydrolysis reaction in an acidic

aqueous solution. The weight average molecular weight of CMC to be hydrolyzed is preferably more than 60,000 and 500,000 or less. If the weight average molecular weight is 500,000 or less, the hydrolysis reaction takes time and it is possible to suppress the occurrence of a large amount of oxidative decomposition products of the CMC. Accordingly, purification becomes easy. The hydrolysis reaction in an acidic aqueous solution proceeds in a short time by heating and pressurizing. The molecular weight of the CMC can be controlled by adjusting the reaction time, temperature, and pH. The reaction can be stopped by cooling and neutralizing with alkali to pH7 or higher. Generally available acids and bases may be used.

[0057] The content of the CMC or its salt is preferably 10 mass% or more and more preferably 20 mass% or more based on the mass of the CNT and carbon black. Further, the content is preferably 100 mass% or less, more preferably 60 mass% or less, and still more preferably 40 mass% or less. By setting the content in the above range, the CNT and carbon black can be satisfactorily and stably present without impairing conductivity when used in the secondary battery electrode. From the viewpoint of coating processability and storage stability, CMC having a higher molecular weight than the CMC used in the dispersion may be added. If CMC having a high molecular weight is added, it is preferably to add the CMC after the CNT dispersion is produced or at the end of the dispersion process. If the CMC is added from the initial stage of the dispersion, defects may occur as follows: the viscosity of the dispersion medium becomes too high and the stirring efficiency deteriorates, or the adsorption equilibrium for the CNT changes and the dispersibility deteriorates.

[Dispersion medium]

[0058] The dispersion medium is water and may optionally include a water-soluble solvent. Examples of the water-soluble solvent include alcohols such as ethanol, propanol, butanol, methyl cellosolve, butyl cellosolve, and propylene glycol monomethyl ether, and N-methyl-2-pyrrolidone (NMP) and the like.

[Other components]

[0059] The conductive material dispersion can be blended with other additives such as a dispersing agent, a wetting agent, an antifoaming agent, a surfactant, a pH adjusting agent, a wetting/penetrating agent, an antioxidant, an antiseptic agent, a fungicidal agent, and a leveling agent; or a water-soluble dispersion medium, a conductive material other than CNT and carbon black, and a polymer component other than CMC when necessary. The blending can be performed appropriately within a range that does not interfere with objects of the embodiments of the present invention. The addition can be performed at any timing such as before preparation of a dispersion element, during dispersion, and after dispersion. As the conductive material other than CNT and carbon black, one or more kinds of carbon materials such as graphite may be used in combination, for example. Polyacrylic acid is preferably used as the pH adjusting agent. Polyacrylic acid having any degree of polymerization can be used and polyacrylic acid may be used as a copolymer with any monomer. Polyacrylic acid may be produced by means of a generally known synthetic method or a commercial product may be used.

[0060] The molecular weight of the polyacrylic acid acting as the pH adjusting agent is not particularly limited. However, the weight average molecular weight is preferably 5,000 to 100,000 and more preferably 10,000 to 50,000.

[0061] It is preferable that the polyacrylic acid acting as the pH adjusting agent is not neutralized. If the carboxyl group is neutralized, the polyacrylic acid generates a phenomenon of counter-ion condensation, and the viscosity of the aqueous solution is remarkably increased. Due to the increase in the viscosity of the aqueous solution, the ease of handling of the conductive material dispersion deteriorates. Additionally, a small amount of water during the preparation of the electrode composition described below is retained even after the drying process, which may affect the performance of the secondary battery.

[0062] The pH of the conductive material dispersion is preferably 7.0 or more and 10.5 or less and preferably 9.0 or more and 10.5 or less. If the pH is in the above range, the conductive material dispersion can be suppressed from becoming gelled easily. In addition, problems such as corrosion of various raw materials and exterior materials in the battery or gelation of the binder can be suppressed. The pH can be measured by using a general pH meter.

[0063] The dispersibility of the conductive material such as the CNT and carbon black in the conductive material dispersion can be evaluated by means of a dynamic viscoelastic measurement using the complex elastic modulus and a phase angle. The complex elastic modulus indicates the hardness of the conductive material dispersion, and the higher the dispersibility of the conductive material and the lower the viscosity of the conductive material dispersion, the smaller the complex elastic modulus. However, suppose that the fiber length of the carbon nanotube is large or the structure length of the carbon black is large. In the above case, even if the conductive material is uniformly and stably dissolved in the medium, the complex elastic modulus may take a high numerical value because of the structural viscosity of the conductive material itself. The phase angle means the phase shift of the stress wave when the strain given to the conductive material dispersion is a sinusoidal wave, that is, the phase angle indicates the ease with which the dispersion is able to flow. In the case of a pure elastic body, the phase angle is 0 degree because the sinusoidal wave has the

same phase with the given strain. Meanwhile, in the case of a pure viscous body, the stress wave is shifted by 90 degrees. In a general viscoelastic measuring sample, a sinusoidal wave has a phase angle which is larger than 0 degree and is smaller than 90 degrees. If the dispersibility of the conductive material in the conductive material dispersion is good, the phase angle approaches 90 degrees of a pure viscous body. However, as similar to the complex elastic modulus, if the conductive material itself has structural viscosity, the phase angle may take a low numerical value even if the conductive material is uniformly and stably dissolved in the medium.

[0064] The complex elastic modulus of the conductive material dispersion is preferably 50 Pa or less, more preferably less than 20 Pa, still more preferably 10 Pa or less, and particularly more preferably 5 Pa or less. The complex elastic modulus of the conductive material dispersion is preferably 0.01 Pa or more, more preferably 0.05 Pa or more, and still more preferably 0.1 Pa or more. The phase angle of the conductive material dispersion is preferably 5 degrees or more, more preferably 19 degrees or more, still more preferably 30 degrees or more, and particularly preferably 45 degrees or more. The phase angle of the conductive material dispersion is preferably 90 degrees or less, more preferably 85 degrees or less, and still more preferably 80 degrees or less. The complex elastic modulus and phase angle can be measured based on the method described in the examples.

[0065] The complex elastic modulus and phase angle of the conductive material dispersion are determined by means of the dispersibility of the CNT and carbon black in the conductive material dispersion, the entanglement of the CNT, carbon black, the CMC, and other resin components, or the influence of the intermolecular forces thereof. From the above, suppose that the complex elastic modulus X (Pa) and the phase angle Y (degree) are set in the above preferred range and the product ($X \times Y$) thereof is 100 or more and 1,500 or less. In the above case, a conductive material dispersion having excellent dispersion stability can be obtained. Furthermore, an electrode film having excellent conductivity can be obtained by forming an excellent conductive network. The CMC having a weight average molecular weight of 10,000 to 150,000 and an etherification degree of 0.5 to 0.9 has a low viscoelasticity. However, suppose that the product ($X \times Y$) of the complex elastic modulus X (Pa) and the phase angle Y (degree) in the case of the conductive material dispersion is 100 or more and 1,500 or less. In the above case, the CMC can perform the role of a thickener or a binder used as the electrode composition of the secondary battery, the electrode strength can be enhanced, and the battery performance can be enhanced. It is more preferable if the complex elastic modulus is 50 Pa or less and the phase angle is 15 degrees or more. It is particularly effective to determine the dispersion state by combining the complex elastic modulus and phase angle with conventional indices such as viscosity, rather than simply requiring that the viscosity of the conductive material dispersion be low and the (apparent) dispersibility be good.

[0066] The dispersibility of the CNT in the conductive material dispersion can also be evaluated by means of the median diameter (μm) which is obtained by using a laser diffraction/scattering type particle size distribution meter. From the median diameter (μm) obtained by using the laser diffraction/scattering type particle size distribution meter, the particle diameter of CNT aggregated particles can be estimated based on the scattered light intensity distribution produced by the particles. The median diameter (μm) is preferably 0.5 μm or more and 5.0 μm or less and more preferably 0.5 μm or more and 2.0 μm or less. The CNT dispersion in an appropriate dispersion state can be obtained by making the median diameter in the above range. CNTs in an aggregated state exist if the median diameter is below the above range. Many finely cut CNTs are generated if the median diameter is above the above range. From the above, it may be difficult to form an efficient conductive network. The median diameter may be measured based on the method described in the examples.

[0067] The dispersibility of the CNT in the conductive material dispersion can also be evaluated by means of gloss measured at 60 degrees (that is, the intensity of the reflected light at 60 degrees relative to the angle of incidence) of a coating film. The coating film is obtained by performing coating on a smooth glass substrate and baking and drying. The coating film is obtained as follows for example: 1 mL of the CNT dispersion is added dropwise onto a smooth glass substrate, coating is performed at 2 cm/sec with a No. 7 bar coater, then baking is performed in a hot air oven at 140 °C for 10 minutes, and cooling is performed, for example. Three locations on the surface of the coating film except the end parts are selected at random by using a gloss meter (gloss meter, micro-gloss 60° manufactured by BYK Gardner) and the average value obtained by measuring each of the three locations once can be used as the gloss at 60 degrees. With respect to the light incident on the coating film, the better the dispersibility, the higher the gloss, because the surface of the coating film becomes smooth. Meanwhile, the lower the dispersibility, the lower the gloss, because light scattering occurs due to the irregularity of the surface of the coating film. The gloss at 60 degrees may be measured based on the method described in the examples. The gloss is preferably 5 or more, more preferably 50 or more, still more preferably 60 or more, and particularly preferably 70 or more. Further, the gloss is preferably 120 or less and more preferably 110 or less. The CNT dispersion in an appropriate dispersion state can be obtained by making the gloss in the above range. CNTs in an aggregated state exist if the gloss is below the above range and many finely cut CNTs are generated if the gloss is above the above range. From the above, it becomes difficult to form an efficient conductive network.

[0068] The TI (thixotropic index) value of the conductive material dispersion can be calculated from the value obtained by dividing the viscosity (mPa·s) at 60 rpm measured by using a B-type viscometer by the viscosity (mPa·s) at 6 rpm. The TI value is preferably 2.0 or more and 5.0 or less. The higher the TI value, the greater the entanglement of the CNT,

carbon black, the CMC, and other resin components, or the structural viscosity resulting from intermolecular forces thereof. The lower the TI value, the lower the structural viscosity. By setting the TI value in the above range, it is possible to suppress the entanglement of the CNT, carbon black, the CMC, and other resin components, and to make these intermolecular forces act appropriately.

5 [0069] The fiber length of the carbon nanotube in the conductive material dispersion is preferably 0.3 to 5 μm and more preferably 0.5 to 3.5 μm .

(Dispersion method)

10 [0070] The conductive material dispersion is preferably produced by finely dispersing the CNT, carbon black, the CMC or its salt, and water after subjecting them to a dispersion treatment by using a dispersing device, for example. In the dispersion treatment, the addition timing of the material to be used may be arbitrarily adjusted and a multistage treatment in which treatment is performed two or more times may be adopted.

15 [0071] Examples of the dispersing device include a kneader, a two-roll mill, a three-roll mill, a planetary mixer, a ball mill, a horizontal sand mill, a vertical sand mill, an annular bead mill, an attriter, a high-shear mixer, a high-pressure homogenizer, an ultrasonic homogenizer, and the like. In particular, it is most preferable to use a high-shear mixer in the initial step of dispersing from the viewpoint of enhancing wetting of the CNT and carbon black and breaking down coarse particles, and then to use a high-pressure homogenizer from the viewpoint of performing dispersing while maintaining the fiber length of the CNT or the structure of carbon black. Further, dispersing is performed by using a high-pressure homogenizer such that the median diameter becomes 4.0 μm or less, and then further dispersing is performed by using a bead mill until the phase angle becomes 40 degrees or more. Accordingly, the dispersion state can be made uniform while maintaining the fiber length. The pressure when the high-pressure homogenizer is used is preferably 60 to 150 MPa and more preferably 60 to 120 MPa.

20 [0072] Examples of dispersing systems using the dispersing device include a batch type dispersion system, a pass type dispersion system, a circulation dispersion system, and the like. Any of them may be used or two or more of them may be used in combination. The batch type dispersion is a method for performing dispersing by using only the dispersing device main body without using piping or the like. Since handling is simple, this method is preferable if a small amount is to be produced. The pass type dispersion system has a tank for supplying a liquid to be dispersed to the dispersing device main body through piping and a tank for receiving the liquid to be dispersed. The system causes the liquid to pass through the dispersing device main body. In the circulation dispersion system, the liquid to be dispersed which has passed through the dispersing device main body is returned to the tank for supplying the liquid to be dispersed, and dispersion is performed while performing circulation. In all of the systems, the dispersing proceeds as the processing time is increased. Therefore, it is sufficient if the passing or circulation is repeated until the desired dispersion state is reached. The processing amount can be increased if the size of the tank or the processing time is changed. The pass type dispersion system is more preferable than the circulation dispersion system because the pass type dispersion system can make the dispersion state uniform easily. The circulation dispersion system is more preferable than the pass type dispersion system because the work and manufacturing equipment are simple. In the dispersion process, the crushing of the aggregated particles, the unraveling, wetting, stabilization, and the like of the CNT proceed sequentially or simultaneously. The finished dispersion state differs depending on the progress method. Therefore, it is preferable to manage the dispersion state in each dispersion process by using various evaluation methods. The states can be managed based on the method described in the examples.

<Composition for secondary battery electrode>

45 [0073] A composition for the secondary battery electrode contains at least the conductive material dispersion, may contain a binder resin, and any component may be further mixed thereto. The composition for the secondary battery electrode contains water and may optionally contain a water-soluble solvent which is exemplified as a dispersion medium.

[Binder resin]

50 [0074] Suppose that the composition for the secondary battery electrode further contains a binder resin. In the above case, there are no particular limitations as long as the resin is normally used as a binder resin for coating materials, and the resin can be appropriately selected depending on the purpose. The binder resin used in the composition for the secondary battery electrode is a resin capable of bonding between materials such as an active material, CNT, carbon black, or other conductive material. The CMC may be a CMC having a different molecular weight, etherification degree, or the like from the CMC contained in the conductive material dispersion. Examples of the binder resin used in the composition for the secondary battery electrode include a polymer or copolymer containing, as constituent units, ethylene, propylene, vinyl chloride, vinyl acetate, vinyl alcohol, maleic acid, acrylic acid, acrylic acid ester, methacrylic acid, meth-

acrylic acid ester, acrylonitrile, styrene, vinyl butyral, vinyl acetal, and vinyl pyrrolidone; a polyurethane resin, a polyester resin, a phenolic resin, an epoxy resin, a phenoxy resin, an urea resin, a melamine resin, an alkyd resin, an acrylic resin, a formaldehyde resin, a silicon resin, and a fluororesin; a cellulose resin; elastomers such as a styrene-butadiene rubber and a fluororubber; and conductive resins such as polyaniline and polyacetylene. A modified product or mixture of these resins and a copolymer may also be used. Among these, when the resin is used as a positive electrode binder resin, a polymer or copolymer having a fluorine atom in a molecule, for example, polyvinylidene fluoride, polyvinyl fluoride, tetrafluoroethylene, or the like is preferable from the viewpoint of resistance. When the resin is used as a negative electrode binder resin, CMC having good adhesion (however, CMC having a different molecular weight, etherification degree, and the like from the CMC contained in the conductive material dispersion), a styrene-butadiene rubber, poly-acrylic acid or the like is preferable.

[0075] The content of the binder resin used in the composition for the secondary battery electrode is preferably 0.5 to 30 mass% and more preferably 0.5 to 25 mass% of the non-volatile content of the composition for the secondary battery electrode.

[0076] The composition for the secondary battery electrode may contain a positive electrode active material or a negative electrode active material. In the present specification, the positive electrode active material and the negative electrode active material may be simply referred to as an "active material". An active material is a material which serves as a basis of a battery reaction. The active material is divided into a positive electrode active material and a negative electrode active material from the electromotive force. In the present specification, the composition for the secondary battery electrode containing the positive electrode active material or the negative electrode active material may be referred to as a "positive electrode mixture composition", a "negative electrode mixture composition" or simply a "mixture composition". The mixture composition is preferably a slurry in order to enhance uniformity and processability. The mixture composition contains at least a conductive material dispersion and an active material and may further contain a binder resin.

[Positive electrode active material]

[0077] The positive electrode active material is not particularly limited, but if the material is used for a secondary battery, the material can be used as a metal compound such as a metal oxide and a metal sulfide capable of reversibly doping or intercalating lithium ions, for example. Examples of the positive electrode active material include composite oxide powders of transition metals and lithium such as lithium manganese complex oxides (for example, $\text{Li}_x\text{Mn}_2\text{O}_4$ or Li_xMnO_2), lithium nickel complex oxides (for example, Li_xNiO_2), lithium cobalt complex oxides (for example, Li_xCoO_2), lithium nickel cobalt complex oxides (for example, $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$), lithium manganese cobalt complex oxides (for example, $\text{Li}_x\text{Mn}_y\text{Co}_{1-y}\text{O}_2$), lithium nickel manganese cobalt complex oxides (for example, $\text{Li}_x\text{Ni}_y\text{Co}_z\text{Mn}_{1-y-z}\text{O}_2$), and spinel-type lithium manganese nickel composite oxides (for example, $\text{Li}_x\text{Mn}_{2-y}\text{Ni}_y\text{O}_4$); lithium phosphate powders having olivine structures (for example, Li_xFePO_4 , $\text{Li}_x\text{Fe}_{1-y}\text{Mn}_y\text{PO}_4$, Li_xCoPO_4 , and the like); transition metal oxide powders such as manganese oxide, iron oxide, copper oxide, nickel oxide, vanadium oxide (for example, V_2O_5 , V_6O_{13}) and titanium oxide; and transition metal sulfide powders such as iron sulfate ($\text{Fe}_2(\text{SO}_4)_3$), TiS_2 , and FeS . The x, y, and z indicate numbers, and the following relationships hold: $0 < x < 1$, $0 < y < 1$, $0 < z < 1$, $0 < y + z < 1$. One or more of the above may be used in combination as the positive electrode active material.

[Negative electrode active material]

[0078] The negative electrode active material is not particularly limited. However, examples of the negative electrode active material include metal oxide systems such as metal Li or an alloy thereof, a tin alloy, a silicon alloy negative electrode, Li_xTiO_2 , $\text{Li}_x\text{Fe}_2\text{O}_3$, $\text{Li}_x\text{Fe}_3\text{O}_4$, Li_xWO_2 capable of reversibly doping or intercalating lithium ions; a conductive polymer such as polyacetylene or poly-p-phenylene; artificial graphite such as a high graphitized carbon material; a carbonaceous powder such as natural graphite; or a resin-fired carbon material. The x indicates a number and $0 < x < 1$ holds. One or more of the above may be used in combination as the negative electrode active material. In particular, if the silicon alloy negative electrode is used, it is preferable to use the silicon alloy negative electrode in combination with artificial graphite such as a high graphitized carbon material, carbonaceous powder such as natural graphite, resin-fired carbon material, and the like because the volume expansion is extremely large while the theoretical capacity is large.

[0079] The content of the conductive material in the mixture composition is preferably 0.01 mass% or more, more preferably 0.02 mass% or more, and still more preferably 0.03 mass% or more relative to the mass of the active material (by assuming that the mass of the active material is 100 mass%). Further, the content is preferably 10 mass% or less, more preferably 5 mass% or less, and still more preferably 3 mass% or less.

[0080] The content of the dispersing agent in the mixture composition is preferably 0.01 mass% or more and more preferably 0.02 mass% or more relative to the mass of the active material (by assuming that the mass of the active material is 100 mass%). The content is preferably 10 mass% or less and more preferably 5 mass% or less.

[0081] Suppose that the mixture composition contains the binder resin. In the above case, the content of the binder resin in the mixture composition is preferably 0.5 mass% or more and more preferably 0.5 mass% or more relative to the mass of the active material (by assuming that the mass of the active material is 100 mass%). Further, the content is preferably 30 mass% or less, more preferably 25 mass% or less, and still more preferably 20 mass% or less.

[0082] The solid content of the mixture composition is preferably 30 mass% or more and more preferably 40 mass% or more relative to the mass of the mixture composition (by assuming that the mass of the mixture composition is 100 mass%). The solid content is preferably 90 mass% or less and more preferably 80 mass% or less.

[0083] The mixture composition can be prepared by means of various conventionally known methods. Examples of the various methods include a method for preparing the composition by adding the active material to the conductive material dispersion; a method for preparing the composition by adding the active material to the conductive material dispersion and then adding the binder resin thereto; and a method for preparing the composition by adding the binder resin to the conductive material dispersion and then adding the active material thereto. As the method for preparing the mixture composition, a method including the dispersion process is preferable. In the method, the binder resin is added to the conductive material dispersion, and then the active material is further added thereto. The dispersing device used for the dispersion is not particularly limited. The mixture composition can be obtained by using the dispersion means cited in the description of the conductive material dispersion. Therefore, in the method for preparing the mixture composition, the dispersion process may be performed by adding an electrode active material without adding the binder resin to the conductive material dispersion.

<Electrode film>

[0084] The electrode film includes at least one selected from the group consisting of a film formed by using the conductive material dispersion and a film formed by using the composition for the secondary battery electrode. The electrode film may further include a current collector. The electrode film can be obtained by coating the composition for the secondary battery electrode on the current collector and drying, for example. The electrode film includes the current collector and the film. An electrode film formed by using the positive electrode mixture composition can be used as a positive electrode. An electrode film formed by using the negative electrode mixture composition can be used as a negative electrode. In the present specification, a film formed by using the composition for the secondary battery electrode containing the active material may be referred to as an "electrode mixture layer".

[0085] The material and shape of the current collector used for forming the electrode film are not particularly limited, and those suitable for various types of secondary batteries can be appropriately selected. Examples of the material of the current collector include a conductive metal such as aluminum, copper, nickel, titanium, or stainless steel or an alloy of a conductive metal. With respect to the shape of the current collector, a flat foil is generally used. However, a current collector having a roughened surface, a holed foil current collector, or a mesh current collector can also be used. The current collector preferably has a thickness of about 0.5 to 30 μm .

[0086] There are no particular limitations regarding the method for coating the conductive material dispersion or the composition for the secondary battery electrode on the current collector, and a known method can be used. Specifically, examples of the method include a die coating method, a dip coating method, a roll coating method, a doctor coating method, a knife coating method, a spray coating method, a gravure coating method, a screen printing method, an electrostatic coating method, or the like. Examples of drying methods include standing drying or drying using a fan dryer, a hot air dryer, an infrared heater, a far-infrared heater, or the like, but the drying methods are not limited to the above.

[0087] After performing coating, a rolling process may be performed by means of a planographic press, a calendar roll, or the like. The thickness of the formed film is 1 μm or more and 500 μm or less and preferably 10 μm or more and 300 μm or less, for example.

[0088] The film formed by using the conductive material dispersion or the composition for the secondary battery electrode can be used as a base layer of the electrode mixture layer in order to enhance the adhesion between the electrode mixture layer and the current collector or to enhance the conductivity of the electrode film.

<Secondary battery>

[0089] The secondary battery includes a positive electrode, a negative electrode, and an electrolyte. At least one selected from the group consisting of the positive electrode and the negative electrode includes an electrode film.

[0090] As the electrolyte, various conventionally known electrolytes in which ions can move can be used. Examples of the electrolyte include, but are not limited to, electrolytes containing lithium salts such as LiBF_4 , LiClO_4 , LiPF_6 , LiAsF_6 , LiSbF_6 , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{LiC}_4\text{F}_9\text{SO}_3$, $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{C}$, LiI , LiBr , LiCl , LiAlCl , LiHF_2 , LiSCN , or LiBPh_4 (where Ph is a phenyl group). The electrolyte is preferably dissolved in a nonaqueous solvent and used as an electrolyte.

[0091] Examples of the nonaqueous solvent includes carbonates such as ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, ethyl methyl carbonate, and diethyl carbonate; lactones such as γ -butyrolactone,

5 γ -valerolactone, and γ -octanoic lactone; glymes such as tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolane, 4-methyl-1,3-dioxolane, 1,2-methoxyethane, 1,2-ethoxyethane, and 1,2-dibutoxyethane; esters such as methyl formate, methyl acetate, and methyl propionate; sulfoxides such as dimethylsulfoxide and sulfolane; nitriles such as acetonitrile, and the like, but the nonaqueous solvent is not particularly limited. Each of these solvents may be used alone or two or more solvents may be used in combination.

10 [0092] A secondary battery (a nonaqueous electrolyte secondary battery) containing a nonaqueous electrolyte solution preferably contains a separator. The nonaqueous electrolyte solution is obtained by dissolving an electrolyte in a non-aqueous solvent. Examples of the separator include, but are not limited to, a polyethylene nonwoven fabric, a polypropylene nonwoven fabric, a polyamide nonwoven fabric, and nonwoven fabrics obtained by subjecting the above nonwoven fabrics to a hydrophilic treatment.

15 [0093] The structure of the nonaqueous electrolyte secondary battery is not particularly limited, but usually a nonaqueous electrolyte secondary battery includes a positive electrode, a negative electrode, and a separator which is provided as needed. The nonaqueous electrolyte secondary battery can be formed into various shapes depending on the purpose of use, such as a paper type, a cylindrical type, a button type, and a laminated type.

15 <Vehicle>

20 [0094] A vehicle includes a secondary battery. The secondary battery can be used as a power source for driving vehicles such as a private car, a bus, a truck, and a train. The secondary battery can be mounted on a hybrid vehicle, an electric vehicle, and the like.

25 [0095] The present invention relates to the subject matter of Japanese Patent Application No. 2020-078026, filed on April 27, 2020 and Japanese Patent Application No. 2020-205488, filed on December 11, 2020, the entire disclosures of which are incorporated herein by reference.

25 [Examples]

30 [0096] The present invention will be described in more detail with reference to the following examples. The present invention is not limited to the following examples provided that the gist of the present invention is not exceeded. Unless otherwise specified, "part" represents "parts by mass" and "%" represents "mass%".

35 (Method for measuring weight average molecular weight (Mw))

40 [0097] The weight average molecular weight (Mw) of the produced carboxymethyl cellulose sodium salt was measured by using gel permeation chromatography (GPC) having an RI detector under the following conditions. The molecular weight is the pullulan equivalent value.

45 Measured sample: 0.1 mass% of aqueous solution

Device: HLC-8320GPC (manufactured by TOSOH CORPORATION)

Eluent: 0.1 M NaCl aqueous solution

45 Column: TSKgel SuperMulti pore PW-M (manufactured by TOSOH CORPORATION)

Flow rate: 1.0 mL/min

Temperature: 25 °C

Injection volume: 100 μ l

45 (Method for measuring etherification degree)

50 [0098] An amount of 0.6 g of carboxymethyl cellulose sodium salt was dried at 105 °C for 4 hours. After the mass of the dried material was weighed, the dried material was wrapped in a filter paper and incinerated in a porcelain crucible. The ash was moved to a 500 ml beaker. Amounts of 250 ml of water and 35 ml of 0.05 mol/l aqueous sulfuric acid solution were added to the ash and the mixture was boiled for 30 minutes. After cooling the mixture, the excess acid was back-titrated by using 0.1 mol/l of aqueous potassium hydroxide solution. Phenolphthalein was used as an indicator. The etherification degree was calculated from the following Formula 1 by using the measured results.

55
$$(\text{Etherification degree}) = 162 \times A / (10,000 - 80A)$$

(Formula 1)

$$A = (af - bf_1) / \text{weight of dried material (g)}$$

A: Amount (ml) of 0.05 mol/l aqueous sulfuric acid solution consumed for binding with alkali in 1 g of sample a:
 Amount (ml) of 0.05 mol/l aqueous sulfuric acid solution used
 f: Potency of 0.05 mol/l aqueous sulfuric acid solution
 b: Titration of 0.1 mol/l aqueous potassium hydroxide solution (ml)
 f₁: Potency of 0.1 mol/l aqueous potassium hydroxide solution

(Preparation of carboxymethyl cellulose sodium salt)

(Production Example 1)

[0099] An amount of 10 parts by mass of a low-density pulp pulverized by using a household mixer was charged into a tank of a planetary mixer (HIVIS DISPER MIX Model 3D-2 manufactured by PRIMIX Corporation). Subsequently, 90 parts by mass of 15 mass% sodium hydroxide/IPA/aqueous solution (the mass ratio of IPA : water is 80:20) was put into the tank, stirred at 40 °C for 150 minutes, and a mercerization reaction was performed to obtain alkali cellulose.

Next, 10 parts by mass of monochloroacetic acid was dissolved in 6 parts by mass of the sodium hydroxide/IPA/aqueous solution. After the temperature was adjusted to 25 °C, alkali cellulose was added over 60 minutes while maintaining the temperature at 35 °C, then the temperature was raised to 80 °C over 30 minutes, and an etherification reaction was performed at 80 °C for 50 minutes. Subsequently, neutralization was performed with 50 mass% of acetic acid and a pH of 7.0 was obtained.

[0100] The solid component of the neutralized product was separated by using a Buchner funnel. Subsequently, 70 mass% aqueous methanol solution was sprinkled on the solid component on the Buchner funnel for washing, and salt, sodium glycolate, and sodium acetate as side products were removed. The product was moved to a stainless steel square tray, dried in a hot air oven at 90 °C for 4 hours, and pulverized. Accordingly, carboxymethyl cellulose sodium salt (CMC 1) was obtained. The weight average molecular weight and the etherification degree of the carboxymethyl cellulose sodium salt obtained were as shown in Table 1.

(Production Examples 2 and 3)

[0101] Carboxymethyl cellulose sodium salts (CMC2 and CMC3) were obtained in the same manner as in Production Example 1 except that the reaction times of the mercerization step and the etherification step were changed to the times shown in Table 1. The weight average molecular weight and the etherification degree of the carboxymethyl cellulose sodium salt obtained were as shown in Table 1.

[Table 1]

[0102]

Table 1

	CMC or its salt	Mercerization step	Etherification step	Weight average molecular weight	Etherification degree
		Reaction time (min)	Reaction time (min)		
Production Example 1	CMC 1	150	50	11,000	0.71
Production Example 2	CMC 2	120	50	24,000	0.67
Production Example 3	CMC 3	50	70	70,000	0.75

(Method for measuring amount of acidic group in CNT)

[0103] The amount of acidic group in the CNT was obtained and calculated as follows by means of back titration from the adsorbed amount of the hexylamine. An amount of 0.2 g of the CNT was collected in a glass bottle (M-70 manufactured by HAKUYO GLASS Co., Ltd.) and 30 ml of hexylamine/NMP solution (0.02 mol/l) was added thereto. The glass bottle was irradiated with ultrasonic waves (frequency: 28 Hz) for 1 hour, and coarse grains were removed by using a nylon

mesh having a mesh opening of 25 μm . Further, centrifugation was performed at 10,000 rpm for 10 minutes by using a centrifuge (mini-centrifuge MCF-1350 (manufactured by LMS)), the supernatant was collected, the filtration was performed by using a membrane filter (filter pore size: 0.22 μm), and the filtrate was collected. An amount of 10 ml of the obtained filtrate was collected and diluted with 40 ml of ion-exchanged water to obtain the titrant. In addition, 10 ml of the hexylamine/NMP solution (0.02 mol/l) not subjected to ultrasonic treatment was diluted with 40 ml of ion-exchanged water together with the CNT to obtain a standard titrant. Each of the titrant and the standard titrant was titrated separately with 0.1 mol/l HCl/ethanol solution by using an automatic potentiometric titrator (AT-710S manufactured by KYOTO ELECTRONICS MANUFACTURING CO., LTD.). The amount of hexylamine adsorbed on the CNT ([hexylamine adsorbed amount] (μmol)) was calculated from the difference in the titration amount at the isoelectric point. With respect to the titrant, 10 ml of the 30 ml hexylamine/NMP solution was collected and the CNT mass was 0.2 g. Therefore, a value obtained by multiplying the [hexylamine adsorbed amount] by 3 and then dividing the resultant value by 0.2 is the [hexylamine adsorbed amount] per unit weight of the conductive material ($\mu\text{mol/g}$). Further, a value obtained by dividing the value by the specific surface area of the CNT is the [hexylamine adsorbed amount] per CNT surface area ($\mu\text{mol/m}^2$).

15 (Method for measuring specific surface area of conductive material)

[0104] After weighing 0.03 g of the conductive material by using an electronic balance (MSA225S100DI manufactured by Sartorius), the conductive material was dried at 110 °C for 15 minutes while degassing. Thereafter, the specific surface area (m^2/g) of the conductive material was measured by using a fully automatic specific surface area analyzer (HM-model 1208 manufactured by MUNTECH).

(Method for measuring G/D ratio of conductive material)

[0105] The conductive material was placed on a Raman microscope (XploRA manufactured by Horiba Seisakusho Co., Ltd.) and the conductive material was measured by using a laser wavelength of 532 nm. The measurement conditions were a capture time of 60 seconds, an integration frequency of 2 times, a dimming filter of 10%, a magnification of the objective lens of 20 times, a focus hole of 500, a slit width of 100 μm , and a measurement wavelength of 100 to 3000 cm^{-1} . The conductive material for measurement was separated onto a glass slide and flattened by using a spatula. The G/D ratio of the conductive material was measured with G being the maximum peak intensity in the range of 1560 to 1600 cm^{-1} in the spectrum and D being the maximum peak intensity in the range of 1310 to 1350 cm^{-1} in the spectrum.

(Method for measuring dispersion grain size)

[0106] The dispersion grain size was obtained based on a determination method in accordance with JIS K5600-2-5 using a grind gauge having a maximum groove depth of 300 μm .

(Method for measuring glossiness)

[0107] A sample for gloss measurement was obtained by adding 1 mL of a conductive material dispersion onto a smooth glass substrate, performing coating by using a No. 7 bar coater at 2 cm/sec, baking in a hot air oven at 140 °C for 10 minutes, and cooling. The coating area was set to about 10 cm × 10 cm. By using a gloss meter (gloss meter, micro-gloss 60° manufactured by BYK Gardner), three locations on the surface of the coating film except the end parts were selected at random and the average value obtained by measuring each of the three locations once was used as the gloss at 60 degrees.

45 (Method for measuring particle size of median diameter of conductive material dispersion)

[0108] The median diameter was measured by using a particle size distribution measuring device (Partical LA-960V2, manufactured by HORIBA). Circulation/ultrasonic wave operating conditions were as follows: circulation speed: 3, ultrasonic intensity: 7, ultrasonic time: 1 minute, stirring speed: 1, and stirring mode: continuous. During air venting, ultrasonic operation was performed at an ultrasonic intensity of 7 and an ultrasonic time of 5 seconds. The refractive index of water was set at 1.333 and the refractive index of the carbon material was set at 1.92. The measurement was performed after diluting the measurement sample such that the transmittance of the red laser diode was 60 to 80%, and the particle size reference was the volume.

55 (Method for measuring viscosity of conductive material dispersion)

[0109] The viscosity of the conductive material dispersion was measured by using a B-type viscometer ("BL" manu-

factured by TOKI SANGYO Co., Ltd.) at a rotor speed of 6 rpm immediately after sufficiently stirring the dispersion element with a spatula at a dispersion temperature of 25 °C by using the B-type viscometer, and then the viscosity was continuously measured at 60 rpm. The lower the viscosity, the better the dispersibility, and the higher the viscosity, the poorer the dispersibility. A clearly separated or precipitated dispersion element was regarded to have poor dispersibility.

5 A TI value was obtained from a value obtained by dividing the viscosity (mPa·s) at 60 rpm by the viscosity (mPa·s) at 6 rpm. The viscosity of the conductive material dispersion is excellent if the viscosity is less than 500 mPa·s, good if the viscosity is 500 mPa·s or more and less than 2,000 mPa·s, bad if the viscosity is 2,000 mPa·s or more and less than 10,000 mPa·s, and extremely bad if the viscosity is 10,000 mPa·s or more and if precipitation or separation occurs.

10 (Measurement of complex elastic modulus and phase angle of conductive material dispersion)

[0110] The complex elastic modulus X and the phase angle Y of the conductive material dispersion were evaluated by performing a dynamic viscoelastic measurement in the range of a strain rate of 0.01% to 5% at 25 °C and a frequency of 1 Hz by using a rheometer (RheoStress 1 rotary rheometer manufactured by Thermo Fisher Scientific Co., Ltd.) with 15 a 2° cone having a diameter of 35 mm. The smaller the complex elastic modulus, the better the dispersibility, and the larger the complex elastic modulus, the worse the dispersibility. The larger the obtained phase angle, the better the dispersibility, and the smaller the phase angle, the worse the dispersibility. Further, the product (X × Y) of the obtained complex elastic modulus X (Pa) and phase angle Y (°) was calculated.

20 (Method for measuring pH of conductive material dispersion)

[0111] The pH of the conductive material dispersion was measured at 25 °C by using a desktop pH meter (Seven-Compact S220 Expert Pro, manufactured by METTLER TOLEDO.).

25 (Method for evaluating stability of conductive material dispersion)

[0112] The storage stability was evaluated by measuring the viscosity of the dispersion element after storage of the element at 50 °C for 7 days. The measurement method was the same as that for the initial viscosity.

30 Determination criteria

[0113]

35 A: equivalent to initial viscosity (excellent)
 B: viscosity slightly changed (good)
 C: viscosity increased but not gelled (possible)
 E: gelled (extremely poor)

40 (Preparation of conductive material dispersion)

[0114] The abbreviations described in the following description are as follows.

- 45 • 10B: JENOTUBE10B (multi-walled CNT manufactured by JEIO, outer diameter 7 to 12 nm, average outer diameter 8.8 nm, specific surface area 230 m²/g, amount of acid group 0.67 μmol/m², 154 μmol/g, G/D ratio 0.80)
- 6A: JENOTUBE6A (multi-walled CNT manufactured by JEIO, outer diameter 5 to 7 nm, average outer diameter 6.9 nm, specific surface area 700 m²/g, amount of acid group 0.27 μmol/m², 190 μmol/g, G/D ratio 0.80)
- TUBALL1: Single wall carbon nanotube (manufactured by OCSiAl, outer diameter 1.3 to 2.3 nm, average outer diameter 1.8 nm, purity 80%, specific surface area 490 m²/g, amount of acid group 0.38 μmol/m², 186 μmol/g, G/D ratio 39.1)
- 50 • TUBALL2: Single wall carbon nanotube (manufactured by OCSiAl, outer diameter 1.2 to 2.0 nm, average outer diameter 1.5 nm, purity 93%, specific surface area 975 m²/g, amount of acid group 0.21 μmol/m², 205 μmol/g, G/D ratio 41.7)
- TNSR: Single wall carbon nanotube (manufactured by Timesnano, outer diameter 1.0 to 2.0 nm, average outer diameter 1.6 nm, specific surface area 610 m²/g, amount of acid group 0.79 μmol/m², 480 μmol/g, G/D ratio 27.8)
- 55 • TNSAR: Single wall carbon nanotube (manufactured by Timesnano, outer diameter 1.0 to 2.0 nm, average outer diameter 1.3 nm, specific surface area 950 m²/g, amount of acid group 0.31 μmol/m², 290 μmol/g, G/D ratio 36.4)
- EC-300J: Ketjen black (manufactured by Lion Specialty Chemicals Co., Ltd., average primary particle diameter 40 nm, specific surface area 800 m²/g, amount of acid group 0.27 μmol/m², 219 μmol/g)

- HS-100: Denka black HS-100 (manufactured by Denka Company Limited. Company Limited., acetylene black, average primary particle diameter 48 nm, specific surface area 39 m²/g, amount of acid group 0.21 μmol/m², 205 μmol/g)
- LITX200: LITX® 200 (manufactured by CABOT CORPORATION., furnace black, specific surface area 130 m²/g)
- LITXHP: LITX® HP (manufactured by CABOT CORPORATION., furnace black, Specific surface area 100 m²/g)
- FX-35: Denka black FX-35 (manufactured by Denka Company Limited., acetylene black, specific surface area 133 m²/g)
- APP-84: carboxymethyl cellulose sodium salt, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., SUN-ROSE A APP-84
- F01MC: carboxymethyl cellulose sodium salt, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., SUN-ROSE F F0 1MC
- F04HC: carboxymethyl cellulose sodium salt, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., SUN-ROSE F F04MC
- A02SH: carboxymethyl cellulose sodium salt, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., SUN-ROSE A02SH
- F10LC: carboxymethyl cellulose sodium salt, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., SUN-ROSE F F10LC
- F10MC: carboxymethyl cellulose sodium salt, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., SUN-ROSE F F10MC
- F30MC: carboxymethyl cellulose sodium salt, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., SUN-ROSE F F30MC
- MAC500LC: carboxymethyl cellulose sodium salt, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., SUNROSE Special Type MAC500LC
- CELLOGEN 5A: carboxymethyl cellulose sodium salt, manufactured by DKS Co., Ltd.
- CELLOGEN 6A: carboxymethyl cellulose sodium salt, manufactured by DKS Co., Ltd.
- PAA: polyacrylic acid, manufactured by Wako Pure Chemical Industries, Ltd., average molecular weight 25,000
- AC-10P: polyacrylic acid, manufactured by TOAGOSEI CO., LTD., average molecular weight 9,000
- AC-10LP: polyacrylic acid, manufactured by TOAGOSEI CO., LTD., average molecular weight 50,000
- HL415: polyacrylic acid, manufactured by Nippon Shokubai, Co., Ltd., Aqualic, average molecular weight 10,000, NV 45%

(Example 1-A1)

[0115] An amount of 93.7 parts by mass of ion-exchanged water was added to a stainless steel container, and 1.25 parts by mass of APP-84 (CMC) was added and dissolved in the water while stirring the water with a disper mixer. Thereafter, 2.0 parts by mass of 10B (CNT) was added to the water while stirring the water with the disper mixer. A square hole high-shear screen was attached to a high-shear mixer (L5M-A, manufactured by SILVERSON), and batch type dispersion was performed at a speed of 8,600 rpm until the entirety became uniform and the dispersion grain size became 250 μm or less by means of a grind gauge. At this time, the dispersion grain size confirmed by using the grind gauge was 180 μm. Subsequently, the liquid to be dispersed was supplied from the stainless steel container to a high-pressure homogenizer (Star Burst Labo HJP-17007, manufactured by SUGINO MACHINE LIMITED.) through piping, and a circulation dispersion treatment was performed. The dispersion treatment was performed by using a single nozzle chamber with a nozzle diameter of 0.25 mm and at a pressure of 100 MPa. After performing dispersing until the viscosity at 60 rpm measured by using a B-type viscometer (VISCOMETER, MODEL: BL manufactured by TOKI SANGYO CO., LTD.) became 3,000 mPa·s or less, 0.5 parts by mass of 10B was further added to the stainless steel container while stirring the mixture with the disper mixer, and a circulation dispersion treatment was performed again by using a high-pressure homogenizer. After performing circulation dispersion by means of a high-pressure homogenizer until the viscosity became 3,000 mPa·s or less, the work of adding 10B to the stainless steel container while stirring the mixture by using the disper mixer was repeated six times in total (the total amount of 10B added was 5.0 parts by mass). Subsequently, a conductive material dispersion (CNT dispersion A1) containing 5.0 parts by mass of the CNT was obtained by performing a pass type dispersion treatment ten times by using the high-pressure homogenizer.

(Examples 1-A2 and 1-A3)

[0116] Conductive material dispersions (CNT dispersions A2 and A3) were obtained in the same manner as in Example 1-A1 except that the number of times the pass type dispersion is performed was changed to 20 times and 30 times.

(Examples 1-A4 to 1-A12 and 1-A17 to 1-A20)

[0117] Conductive material dispersions (CNT dispersions A4 to A20) were obtained in the same manner as in Example 1-1A except that the material, composition ratio, and the number of times the pass type dispersion is performed shown in Table 3 were changed.

(Comparative Examples 1-a1 to 1-a14)

[0118] Conductive material dispersions (CNT dispersions a1 to a14) were obtained in the same manner as in Example 1-1A except that the material, composition ratio, and the number of times the pass type dispersion is performed shown in Table 4 were changed.

(Example 1-A13)

[0119] The conductive material dispersion (a CNT dispersion A3) obtained in Example 1-A3 was introduced into a stainless steel container, and 0.004 parts by mass of PAA was added while stirring the mixture with a disper mixer, and accordingly a conductive material dispersion (a CNT dispersion A13) containing 5.0 parts by mass of the CNT was obtained. The pH of CNT dispersion A13 was 7.5.

(Example 1-A14)

[0120] A conductive material dispersion (a conductive material dispersion A14) was obtained by means of the same method as in Example 1-A13 except that PAA was changed to AC-10P. The pH of the CNT dispersion A14 was 7.1.

(Example 1-A15)

[0121] A conductive material dispersion (a CNT dispersion A15) was obtained by means of the same method as in Example 1-A13 except that PAA was changed to AC-10 LP. The pH of the CNT dispersion A15 was 7.0.

(Example 1-A16)

[0122] A conductive material dispersion (a CNT dispersion A16) was obtained by means of the same method as in Example 1-A13 except that the PAA was changed to HL415. The pH of the CNT dispersion A16 was 7.5.

(Example 1-A21)

[0123] An amount of 98.05 parts by mass of ion-exchanged water was added to a stainless steel container, and 0.45 parts by mass of APP-084 (CMC) was added and dissolved in the water while stirring the water with a disper mixer. Thereafter, 0.115 parts by mass of TNSR (CNT) and 1.385 parts by mass of 10B (CNT) were added to the water while stirring the water with the disper mixer. A square hole high-shear screen was attached to a high-shear mixer (L5M-A, manufactured by SILVERSON) and batch type dispersion was performed at a speed of 8,600 rpm until the entirety became uniform and the dispersion grain size became 250 μm or less by using a grind gauge. Subsequently, the liquid to be dispersed was supplied from the stainless steel container to a high-pressure homogenizer (Star Burst Labo HJP-17007, manufactured by SUGINO MACHINE LIMITED.) via piping, and a pass type dispersion treatment was performed 20 times. The dispersion treatment was performed by using a single nozzle chamber with a nozzle diameter of 0.25 mm at a pressure of 100 MPa, and accordingly a conductive material dispersion (a CNT dispersion A21) containing 1.5 parts by mass of the CNT was obtained. The CNT mass ratio of TNSR to 10B was 1:12.

(Example 1-A22)

[0124] A conductive material dispersion (a CNT dispersion A22) containing 2.5 parts by mass of the CNT was obtained by means of the same method as in Example 1-A21 except that the addition amount of ion-exchanged water was changed from 98.05 parts by mass to 96.75 parts by mass, the addition amount of APP-084 was changed from 0.45 parts by mass to 0.75 parts by mass, the addition amount of 10B was changed from 1.385 parts by mass to 2.4 parts by mass, and the addition amount of TNSR was changed from 0.115 parts by mass to 0.1 parts by mass. The CNT mass ratio of the TNSR to 10B was 1:24.

(Example 1-A23)

[0125] An amount of 98.64 parts by mass of ion-exchanged water was added to a stainless steel container and 0.56 parts by mass of APP-084 (CMC) was added and dissolved in the water while stirring the water with a disper mixer. Thereafter, 0.062 parts by mass of TNSR (CNT) and 0.738 parts by mass of 6A (CNT) were added to the water while stirring the water with the disper mixer. A square hole high-shear screen was attached to a high-shear mixer (L5M-A, manufactured by SILVERSON) and batch type dispersion was performed at a speed of 8,600 rpm until the entirety became uniform and the dispersion grain size became 250 μm or less by means of a grind gauge. Subsequently, the liquid to be dispersed was supplied from the stainless steel container to a high-pressure homogenizer (Star Burst Labo HJP-17007, manufactured by SUGINO MACHINE LIMITED.) via piping, and the pass type dispersion treatment was performed 20 times. The dispersion treatment was performed by using a single nozzle chamber with a nozzle diameter of 0.25 mm at a pressure of 100 MPa, and accordingly a conductive material dispersion (a CNT dispersion A23) containing 1.0 parts by mass of the CNT was obtained. The CNT mass ratio of TNSR to 6A was 1:12.

(Example 1-A24)

[0126] A conductive material dispersion (a CNT dispersion A24) containing 2.5 parts by mass of the CNT was obtained by means of the same method as in Example 1-A23 except that the addition amount of ion-exchanged water was changed from 98.64 parts by mass to 98.3 parts by mass, the addition amount of APP-084 was changed from 0.56 parts by mass to 0.70 parts by mass, the addition amount of 6A was changed from 0.738 parts by mass to 0.96 parts by mass, and the addition amount of TNSR was changed from 0.062 parts by mass to 0.04 parts by mass. The CNT mass ratio of TNSR to 6A was 1:24.

(Example 1-A25)

[0127] A conductive material dispersion (a CNT dispersion A25) containing 1.1 parts by mass of the CNT was obtained by means of the same method as in Example 1-A23 except that the addition amount of ion-exchanged water was changed from 98.64 parts by mass to 98.13 parts by mass, the addition amount of APP-084 was changed from 0.56 parts by mass to 0.77 parts by mass, the addition amount of 6A was changed from 0.738 parts by mass to 1.08 parts by mass, and the addition amount of TNSR was changed from 0.062 parts by mass to 0.02 parts by mass. The CNT mass ratio of TNSR to 6A was 1:48.

(Comparative Example 1-a15)

[0128] The conductive material dispersion (the CNT dispersion A3) obtained in Examples 1-A3 was introduced into a stainless steel container, and while stirring the dispersion with a disper mixer, 0.04 parts by mass of PAA relative to the mass of the CNT was added to the dispersion. Accordingly, a conductive material dispersion (a CNT dispersion a15) containing 5.0 parts by mass of the CNT was obtained. The pH of the CNT dispersion a15 was 5.5.

(Comparative Example 1-a16 to 1-a17)

[0129] Dispersions (CB Dispersions a1 to a2) were obtained in the same manner as in Example 1-1 A except that the material, composition ratio, and number of times the pass type dispersion is performed shown in Table 4 were changed.

(Examples 1-B1 to 1-B3)

[0130] An amount of 80 parts by mass of the conductive material dispersions (the CNT dispersions A1 to A3) obtained in Examples 1-A1 to 1-A3 was introduced into a glass bottle (M-140, manufactured by HAKUYO GLASS Co., Ltd.) and 140 parts by mass of zirconia beads (bead diameter 1.0 mm ϕ) was added. After performing dispersing for two hours by using a paint conditioner manufactured by Red Devil Equipment Co., the zirconia beads were separated, and conductive material dispersions (CNT dispersions B1 to B3) were obtained.

(Example 1-B4)

[0131] An amount of 80 parts by mass of the conductive material dispersion (CNT dispersion A3) obtained in Example 1-A3 was introduced into a glass bottle (M-140, manufactured by HAKUYO GLASS Co., Ltd.) and 0.012 parts by mass of MAC500LC and 140 parts by mass of zirconia beads (bead diameter 1.0 mm ϕ) were added. After performing dispersing for 5 hours by using a paint conditioner manufactured by Red Devil Equipment Co., the zirconia beads were

separated and a conductive material dispersion (conductive material dispersion B4) was obtained.

(Examples 1-C1 to 1-C3)

5 [0132] The conductive material dispersions obtained in Examples 1-A1 to 1-A3 (CNT dispersions A1 to A3) were introduced into a stainless steel container and diluted with ion-exchanged water while being stirred by using a disper mixer. Accordingly, conductive material dispersions (CNT dispersions C1 to C3) containing 2.0 parts by mass of the CNT were obtained.

10 (Examples 1-D1 to 1-D3)

15 [0133] Amounts of 2.0 parts by mass of 10B (CNT), 0.5 parts by mass of CMC shown in Table 3, 97.6 parts by mass of ion-exchanged water, and 140 parts by mass of zirconia beads (bead diameter 0.5 mmcp) were charged into a glass bottle (M-140, manufactured by HAKUYO GLASS Co., Ltd.). After performing dispersing for 4 hours by using a paint conditioner manufactured by Red Devil Equipment Co., the zirconia beads were separated and conductive material dispersions (CNT dispersions D1 to D3) were obtained.

(Example 1-D4)

20 [0134] An amount of 97.6 parts by mass of ion-exchanged water was added to a stainless steel container and 0.4 parts by mass of F10LC (CMC) was added and dissolved into the water while stirring the water by using a disper mixer. Thereafter, 1.5 parts by mass of 10B (CNT) was added while stirring the mixture with the disper mixer. A square hole high-shear screen was attached to a high-shear mixer (L5M-A, manufactured by SILVERSON) and batch type dispersion was performed at a speed of 8,600 rpm until the entirety became uniform and the dispersion grain size became 250 μm or less by means of a grind gauge. The dispersion was performed until the viscosity at 60 rpm as measured by using a B-type viscometer (VISCOMETER, MODEL: BL manufactured by TOKI SANGYO CO., LTD.,) of the liquid to be dispersed was 3,000 mPa·s or less. Thereafter, 0.5 parts by mass of 10B was further added to the stainless steel container while stirring the mixture with the disper mixer and a pass type dispersion treatment was performed ten times with a high-pressure homogenizer. Accordingly, a conductive material dispersion (a CNT dispersion D4) containing 2.0 parts by mass of the CNT was obtained.

(Example 1-E1)

35 [0135] An amount of 83.5 parts by mass of ion-exchanged water was added to a stainless steel container and 1.5 parts by mass of APP-84 (CMC) was added and dissolved into the water while stirring the water with a disper mixer. Thereafter, 10 parts by mass of LITX200 (furnace black) was added to the mixture while stirring the mixture with the disper mixer. A square hole high-shear screen was attached to a high-shear mixer (L5M-A, manufactured by SILVERSON) and batch type dispersion was performed at a speed of 8,600 rpm until the entirety became uniform and the dispersion grain size became 250 μm or less by means of a grind gauge. Subsequently, the liquid to be dispersed was supplied from the stainless steel container to a high-pressure homogenizer (Star Burst Labo HJP-17007, manufactured by SUGINO MACHINE LIMITED.) through piping and a circulation dispersion treatment was performed. The dispersion treatment was performed by using a single nozzle chamber with a nozzle diameter of 0.25 mm at a pressure of 100 MPa. After performing dispersing until the viscosity at 60 rpm measured by using a B-type viscometer of the liquid to be dispersed (VISCOMETER, MODEL: BL manufactured by TOKI SANGYO CO., LTD.) was 1,000 mPa·s or less, 1 part by mass of LITX200 was further added to the stainless steel container while stirring the mixture with the disper mixer and a circulation dispersion treatment was performed again by using the high-pressure homogenizer. After performing circulation dispersion by using the high-pressure homogenizer until the viscosity became 1,000 mPa·s or less, the work of adding LITX200 to the stainless steel container while stirring the mixture by using the disper mixer was repeated 5 times in total (the total amount of LITX200 added was 15 parts by mass). Subsequently, the pass type dispersion treatment was performed 3 times by using the high-pressure homogenizer, and accordingly a conductive material dispersion (CB Dispersion E1) containing 15 parts by mass of LITX200 was obtained.

(Examples 1-E2 to 1-E3)

55 [0136] Conductive material dispersions (CB Dispersion E2 to E3) were obtained in the same manner as in Examples 1-E1 except that the material was changed to the conductive material shown in Table 3.

(Comparative Examples 1-d1 to 1-d3)

[0137] Conductive material dispersions (CNT dispersions d1 to d3) were obtained in the same manner as in Examples 1-D1 except that the materials were changed to the materials shown in Table 4.

[0138] The weight average molecular weight and the etherification degree of carboxymethyl cellulose or its salt used in the examples and comparative examples were as shown in Table 2. The weight average molecular weight and the etherification degree were calculated based on the same measurement method as in the production example.

[Table 2]

[0139]

Table 2

Commercially available CMC	Weight average molecular weight	Etherification degree
APP-84	18,000	0.71
CELLOGEN 5A	13,000	0.75
CELLOGEN 6A	23,000	0.73
F01 MC	56,000	0.68
F04HC	68,000	0.93
A02SH	100,000	1.46
F10LC	123,000	0.60
F10MC	126,000	0.71
F30MC	149,000	0.69
MAC500LC	349,000	0.70

[Table 3]

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Table 3

Conductive material dispersion	Pass type dispersion	Conductive material		CMC	Initial viscosity		pH	Glossiness	Median diameter (μm)	Complex elastic modulus X (Pa)	Phase angle Y (°)	Product (X × Y)			
		Type	Amount added (Parts)		Type	Amount added to CNT (parts)									
Example 1-A1	CNT dispersion A1	10B	5.0	APP-084	20.0	30,000	6,100	4.92	C	9.63	76.9	0.90	42.70	26.70	1140
Example 1-A2	CNT dispersion A2	10B	5.0	APP-084	20.0	12,200	2,800	4.36	C	9.64	90.2	0.84	19.80	34.90	691
Example 1-A3	CNT dispersion A3	10B	5.0	APP-084	20.0	12,900	2,400	5.38	B	960	93.3	0.73	15.60	36.40	568
Example 1-A4	CNT dispersion A4	6A	1.2	APP-084	62.5	22,000	4,800	4.58	C	1000	58.7	0.95	43.10	18.50	797
Example 1-A5	CNT dispersion A5	6A	1.2	APP-084	62.5	5,500	1,460	3.77	B	10.10	70.2	0.77	10.10	33.10	334
Example 1-A6	CNT dispersion A6	6A	1.2	APP-084	62.5	2,900	860	3.37	B	10.10	76.5	0.71	4.74	42.70	202
Example 1-A7	CNT dispersion A7	TUBALL 1	0.4	APP-084	100.0	4,300	1,330	3.23	B	960	87.5	1.50	5.30	43.10	228
Example 1-A8	CNT dispersion A8	TUBALL 2	0.4	APP-084	100.0	5,200	1,780	292	B	9.50	83.2	1.43	5.10	41.50	212
Example 1-A9	CNT dispersion A9	10B	5.0	F01MC	20.0	36,800	8,600	4.28	C	9.50	68.8	1.30	55.30	25.50	1410
Example 1-A 10	CNT dispersion A10	10B	5.0	CMC 1	20.0	24,500	5,100	4.80	C	9.60	82.1	0.92	38.80	28.70	1114
Example 1-A11	CNT dispersion A11	10B	5.0	CMC 2	20.0	33,600	6,780	4.96	C	9.60	71.5	0.96	48.60	25.80	1254
Example 1-A 12	CNT dispersion A12	10B	5.0	CMC 3	20.0	42,500	9,800	4.34	C	9.60	66.3	1.42	59.60	25.10	1496

5 10 15 20 25 30 35 40 45 50 55

(continued)

Conductive material dispersion	Pass type dissersion	Conductive material		CMC		Initial viscosity		TI val- ue	Stability	pH	Glossiness	Median diameter (μm)	Complex elastic modulus X (Pa)	Phase angle Y ()	Product (X \times Y)
		Number of times (time)	Type	Amount added (Parts)	Type	Amount added to CNT (parts)	6rpm (mPa·s)								
Example CNT dispersion A13	30	10B	5.0	CMC 3	20.0	13,000	2.800	4.64	C	7.50	90.3	0.80	2000	3300	660
Example CNT dispersion A14	30	10B	5.0	CMC 3	20.0	10,800	2200	4.90	C	7.10	92.5	0.75	23.20	28.50	661
Example CNT dispersion A15	30	10B	5.0	CMC 3	20.0	11,000	2,300	4.78	C	700	93.1	0.77	22.50	28.70	646
Example CNT dispersion A16	30	10B	5.0	CMC 3	20.0	13,500	2,900	4.66	C	7.50	91.6	0.80	20.30	32.20	654
Example CNT dispersion A17	10	10B	5.0	CELLOGEN 5A	20.0	26,000	5,300	4.91	C	9.50	78.5	0.85	38.50	30.30	1167
Example CNT dispersion A18	10	10B	5.0	CELLOGEN 6A	1500	32,000	5,800	5.52	C	9.50	70.2	0.92	45.50	10.10	460
Example CNT dispersion A19	20	TNSR	0.4	APP-084	1500	2,000	500	400	B	9.40	88.1	1.21	12.10	35.20	426
Example CNT dispersion A20	20	TNSAR	0.4	APP-084	300	3800	1,130	3.36	B	9.50	85.3	1.53	10.50	38.80	407
Example CNT dispersion A21	20	10B/ TNSR	1.5	APP-084	300	11,500	1,650	7.00	C	9.60	88.3	1.43	46.60	9.30	433
Example CNT dispersion A22	20	10B/ TNSR	2.5	APP-084	700	21,500	3,350	6.42	C	9.60	89.5	1.15	117.70	8.60	1012
Example CNT dispersion A23	20	6A/TNSR	0.8	APP-084	700	2,230	530	4.20	B	9.90	71.5	1.50	3.20	33.80	108
Example CNT dispersion A24	20	6A/TNSR	1.0	APP-084	70.0	2,680	700	3.80	B	10.00	70.8	0.95	3.20	37.80	121

55 50 45 40 35 30 25 20 15 10 5

(continued)

Conductive material dispersion	Pass type disoersion	Conductive material		CMC		Initial viscosity		TI value	Stability	pH	Glossiness	Median diameter (μm)	Complex elastic modulus X (Pa)	Phase angle Y ()	Product (X × Y)
		Number of times (time)	Type	Amount added (Parts)	Type	Amount added to CNT (parts)	6rpm (mPa·s)								
Example CNT dispersion A25	30	6ATNSR	1.1	APP-084	700	3,600	930	3.87	B	10.10	752	0.78	5.10	40.90	209
Example CNT dispersion B1	10	10B	5.0	APP-084	20.0	3,000	830	3.61	B	9.50	98.3	0.71	11.30	40.90	462
Example CNT dispersion B2	20	10B	5.0	APP-084	20.0	2,000	790	2.53	A	9.50	99.9	0.39	8.93	44.90	401
Example CNT dispersion B3	30	10B	5.0	APP-084	20.0	860	366	2.35	A	9.50	98.9	1.59	5.06	53.70	272
Example CNT dispersion B4	30	10B	5.0	APP-084	20.0	42,400	9,700	4.37	C	9.60	92.1	0.81	45.00	26.00	1170
Example CNT dispersion C1	10	10B	20	APP-084	20.0	1,210	290	4.17	A	9.40	96.6	0.96	5.50	65.10	358
Example CNT dispersion C2	20	10B	20	APP-084	20.0	1050	260	404	A	9.40	97.6	0.77	5.20	70.30	366
Example CNT dispersion C3	30	10B	20	APP-084	20.0	930	240	3.88	A	9.40	96.4	0.71	4.20	74.40	312
Example CNT dispersion D1	-	10B	20	APP-084	20.0	1,440	347	4.16	B	9.70	10.0	5.14	13.80	8.28	114
Example CNT dispersion D2	-	10B	20	F01 MC	20.0	1,450	322	450	B	9.87	8.0	8.25	21.80	709	155
Example CNT dispersion D3	-	10B	20	CMC 1	20.0	1,280	298	430	B	9.70	10.8	4.30	12.20	1050	128
Example CNT dispersion D4	-	10B	20	F10LC	20.0	12,200	2,500	4.88	C	9.70	7.1	7.50	3080	5.60	172

(continued)

Conductive material dispersion	Pass type-disoersion	Conductive material		CMC	Initial viscosity		pH	Glossiness	Median diameter (μm)	Complex elastic modulus X (Pa)	Phase angle Y (°)	Product (X × Y)
		Type	Amount added (Parts)		Type	Amount added to CNT (parts)						
Example 1-E1	CB dispersion E1	5	LITX200	150	APP-084	10.0	1,200	280	4.29	B	9.80	83.5
Example 1-E2	CB dispersion E2	5	LITXHP	150	APP-084	10.0	1.550	350	4.43	B	9.80	82.8
Example 1-E3	CB dispersion E3	5	FX35	150	APP-084	10.0	1.500	380	3.95	B	9.60	81.8

[Table 4]

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Table 4

Conductive material dispersion	Pass type	CNT · Conductive material	CMC	Initial viscosity	TI value	Stability	pH	Glossiness	Median diameter (μm)	Complex elastic modulus X (Pa)	Phase angle Y (°)	Product (X × Y)
	Conductive material dispersion	Number of times (time)	Amount added (Parts)	Type	Amount added to CNT (parts)	6 rpm (mPa·s)	60 rpm (mPa·s)					
Comparative Example 1-a1	CNT dispersion a1	1	10B	5.0	APP-084	20	53,400	10,000 or more	-	E	960	54.10
Comparative Example 1-a2	CNT dispersion a2	3	10B	5.0	APP-084	20	44,500	10,000 or more	-	E	960	55.50
Comparative Example 1-a3	CNT dispersion a3	5	10B	5.0	APP-084	20	33,600	7,800	4.31	E	9.60	56.20
Comparative Example 1-a4	CNT dispersion a4	1	6A	1.2	APP-084	62.5	21,600	5,190	4.16	E	10.20	Formation of coating film not possible
Comparative Example 1-a5	CNT dispersion a5	3	6A	1.2	APP-084	62.5	39,800	10,000 or more	-	E	1020	40.00
Comparative Example 1-a6	CNT dispersion a6	5	6A	1.2	APP-084	62.5	94,300	10,000 or more	-	E	10.20	48.80
												609.60
												5.45
												33322
												2720

(continued)

Conductive material dispersion	Pass type dispersion	CNT · Conductive material		CMC		Initial viscosity		pH	Glossiness	Median diameter (μm)	Complex elastic modulus X (Pa)	Phase angle Y (°)	Product (X \times Y)
		Number of times (time)	Amount added (Parts)	Type	Amount added to CNT (parts)	6rpm (mPa·s)	60rpm (mPa·s)						
Comparative Example 1- a7	CNT dispersion a7	10	10B	5.0	A02SH	20	53,400	6,900	7.74	E	9.70	Formation of coating film not possible	5.80
Comparative Example 1- a8	CNT dispersion a8	20	10B	5.0	A02SH	20	69,800	7,920	8.81	E	9.70	5212	4.65
Comparative Example 1- a9	CNT dispersion a9	30	10B	5.0	A02SH	20	97,500	10,000 or more	-	E	9.70	59.04	4.54
Comparative Example 1- a10	CNT dispersion a10	20	10B	5.0	F04HC	20	27,310	4,460	6.12	C	10.11	4.73	5.61
Comparative Example 1- a11	CNT dispersion a11	20	10B	5.0	F10LC	20							
Comparative Example 1- a12	CNT dispersion a12	20	10B	5.0	F10MC	20							
Comparative Example 1- a13	CNT dispersion a13	20	10B	5.0	F30MC	20							
Comparative Example 1- a14	CNT dispersion a14	20	10B	5.0	MAC500LC	20							

Preparation of dispersion not possible (viscosity was high and CNT concentration did not reach 5%)

(continued)

Conductive material dispersion	Pass type dispersion	CNT · Conductive material		CMC		Initial viscosity		pH	Glossiness	Median diameter (µm)	Complex elastic modulus X (Pa)	Phase angle Y (°)	Product (X × Y)
		Number of times (time)	Type	Amount added (Parts)	Type	Amount added to CNT (parts)	6 rpm (mPa·s)						
Comparative Example 1-a15	CNT dispersion a15	30	10B	5.0	APP-084	20.0	62,400	10,000 or more	-	E	550	Formation of coating film not possible	502.00 4.70 2359
Comparative Example 1-a16	CB dispersion a1	5	HS-100	20.0	A02SH	5	360	140	2.57	C	8.30	36.30	5.10 0.43 60.20 26
Comparative Example 1-a17	CB dispersion a2	10	EC-300J	5.0	A02SH	20	2,200	560	3.93	C	8.50	18.10	6.80 133.10 15.30 2036
Comparative Example 1-d1	CNT dispersion b1	-	10B	2.0	F10LC	20	26,870	5,460	4.92	E	8.50	3.27	4.51 389.10 7.80 3035
Comparative Example 1-d2	CNT dispersion b2	-	10B	2.0	F10MC	20	25,110	5,120	4.90	E	9.79	3.50	4.80 447.10 7.68 3434
Comparative Example 1-d3	CNT dispersion b3	-	10B	2.0	F30MC	20	31,650	6,630	4.77	E	9.18	2.61	5.30 409.50 9.21 3771

*CNT dispersion a15 further contains 0.04 parts by mass of PAA

(Preparation of negative electrode mixture composition and negative electrode)

[0142] The abbreviations described in the following description are as follows.

- 5 • Silicon: silicon monoxide (SILICON MONOOXIDE SiO 1.3C 5 μm , non-volatile content 100%, manufactured by Osaka Titanium Technologies Co., Ltd.)
- Artificial graphite: CGB-20 (manufactured by Nippon Graphite Industries, Co., Ltd., non-volatile content 100%)
- MAC500LC: carboxymethyl cellulose sodium salt, SUNROSE Special Type, MAC500LC (manufactured by NIPPON PAPER INDUSTRIES CO., LTD., non-volatile content 100%)
- 10 • SBR: styrene-butadiene rubber TRD2001 (manufactured by JSR CORPORATION, non-volatile content 48%)

(Example 2-A1)

15 [0143] A CNT dispersion (a CNT dispersion A1), MAC500LC (CMC), and water were added to a plastic container having a capacity of 150 cm^3 . Thereafter, the mixture was stirred at 2,000 rpm for 30 seconds by using a rotation/revolution mixer (Awa-tori Rentaro, ARE-310 manufactured by THINKY CORPORATION). After adding artificial graphite and silicon as the negative electrode active materials, the mixture was stirred at 2,000 rpm for 150 seconds by using the rotation/revolution mixer. Thereafter, SBR was added, and the mixture was stirred at 2,000 rpm for 30 seconds by using the rotation/revolution mixer. Accordingly, a negative electrode mixture composition was obtained. The non-volatile content 20 of the negative electrode mixture composition was 48 mass%. The ratio of artificial graphite : silicon : CNT : CMC (MAC500LC): non-volatile content of SBR in the non-volatile content of the negative electrode mixture composition was 87:10:0.5:1:1.5.

25 [0144] The obtained negative electrode mixture composition was coated on a copper foil having a thickness of 20 μm by using an applicator and the coating film was dried at $120^\circ\text{C} \pm 5^\circ\text{C}$ for 25 minutes in an electric oven. Accordingly, an electrode film was prepared. Thereafter, the electrode film was rolled by using a roll press (3t hydraulic roll press manufactured by THANK METAL CO., LTD.) and a negative electrode (a negative electrode A1) was obtained. The weight per unit of the mixture layer was 10 mg/cm^2 . The density of the mixture layer after performing a rolling treatment was 1.6 g/cc.

30 (Examples 2-A2 to 2-A25, 2-B1 to 2-B4, 2-C1 to 2-C3, 2-D1 to 2-D4, 2-E1 to 2-E3, and Comparative Examples 2-a1 to 2-a17, and 2-d1 to 2-d3)

35 [0145] Negative electrodes A2 to A25, negative electrodes B1 to B3, negative electrodes C1 to C3, negative electrodes D1 to D4, negative electrodes E1 to E3, negative electrodes a1 to a17, and negative electrodes d1 to d3 were obtained by means of the same method as in Example 2-A1 except that the CNT dispersions were changed to the CNT dispersions shown in Table 5 (CNT dispersions A2 to A25, CNT dispersions B1 to B4, CNT dispersions C1 to C3, CNT dispersions D1 to D4, CB Dispersions E1 to E3, CNT dispersions a1 to a15, CB Dispersions a1 and a2, and CNT dispersions d1 to d3).

40 (Method for evaluating conductivity of negative electrode)

45 [0146] With respect to the obtained negative electrode, the surface resistivity (Ω/\square) of the mixture layer was measured by using Loresta GP, MCP-T610 manufactured by Mitsubishi Chemical Analytech Co., Ltd. After the measurement, the value was multiplied by the thickness of the mixture layer, and the resultant value was set as the volume resistivity ($\Omega\cdot\text{cm}$) of the negative electrode. With respect to the thickness of the mixture layer, the thickness of the copper foil was subtracted from the average value obtained by measuring three locations in the electrode by using a film thickness meter (DIGIMICRO MH-15M manufactured by NIKON CORPORATION), and the resultant value was set as the volume resistivity ($\Omega\cdot\text{cm}$) of the negative electrode.

Determination criteria

50 [0147]

- A: Less than 0.3 $\Omega\cdot\text{cm}$ (Excellent)
- B: 0.3 $\Omega\cdot\text{cm}$ or more and less than 0.5 $\Omega\cdot\text{cm}$ (Good)
- 55 C: 0.5 $\Omega\cdot\text{cm}$ or more (Poor)

(Method for evaluating adhesion of negative electrode)

[0148] The obtained negative electrode was cut into two rectangles of 90 mm × 20 mm with the coating direction as the major axis. The peel strength was measured by using a tabletop tensile testing machine (Strograph E3 manufactured by Toyo Seiki Manufacturing Co.) and evaluated based on the 180-degree peel test method. Specifically, a 100 mm × 30 mm size double-sided tape (No. 5000NS, manufactured by Nitoms, Inc.) was stuck on a stainless plate, and the mixture layer side of the prepared negative electrode was brought into close contact with the other side of the double-sided tape to obtain a test sample. Next, the test sample was fixed vertically such that the short sides of the rectangle became the upside and the downside. Peeling was performed while pulling the end of the copper foil upward from the lower side at a constant speed (50 mm/min). The mean value of the stress at this time was defined as the peel strength.

Determination criteria

[0149]

A: 0.5 N/cm or more (Excellent)
 B: 0.1 N/cm or more and less than 0.5 N/cm (Good)
 D: Less than 0.1 N/cm (Poor)

[Table 5]

[0150]

Table 5

	Negative electrode	Conductive material dispersion	Volume resistivity	Peel strength
Example 2-A1	Negative electrode A1	CNT dispersion A1	B	B
Example 2-A2	Negative electrode A2	CNT dispersion A2	B	B
Example 2-A3	Negative electrode A3	CNT dispersion A3	A	B
Example 2-A4	Negative electrode A4	CNT dispersion A4	B	B
Example 2-A5	Negative electrode A5	CNT dispersion A5	A	B
Example 2-A6	Negative electrode A6	CNT dispersion A6	A	A
Example 2-A7	Negative electrode A7	CNT dispersion A7	A	A
Example 2-A8	Negative electrode A8	CNT dispersion A8	A	A
Example 2-A9	Negative electrode A9	CNT dispersion A9	B	B
Example 2-A10	Negative electrode A10	CNT dispersion A10	A	B
Example 2-A11	Negative electrode A11	CNT dispersion A11	B	B
Example 2-A12	Negative electrode A12	CNT dispersion A12	B	B

(continued)

		Negative electrode	Conductive material dispersion	Volume resistivity	Peel strength
5	Example 2-A13	Negative electrode A13	CNT dispersion A13	A	B
10	Example 2-A14	Negative electrode A14	CNT dispersion A14	A	B
15	Example 2-A15	Negative electrode A15	CNT dispersion A15	A	B
20	Example 2-A16	Negative electrode A16	CNT dispersion A16	A	A
25	Example 2-A17	Negative electrode A17	CNT dispersion A17	A	B
30	Example 2-A18	Negative electrode A18	CNT dispersion A18	A	B
35	Example 2-A19	Negative electrode A19	CNT dispersion A19	A	A
40	Example 2-A20	Negative electrode A20	CNT dispersion A20	A	A
45	Example 2-A21	Negative electrode A21	CNT dispersion A21	A	A
50	Example 2-A22	Negative electrode A22	CNT dispersion A22	A	A
55	Example 2-A23	Negative electrode A23	CNT dispersion A23	A	A
	Example 2-A24	Negative electrode A24	CNT dispersion A24	A	A
	Example 2-A25	Negative electrode A25	CNT dispersion A25	A	A
	Example 2-B1	Negative electrode B1	CNT dispersion B1	B	A
	Example 2-B2	Negative electrode B2	CNT dispersion B2	A	A
	Example 2-B3	Negative electrode B3	CNT dispersion B3	A	A
	Example 2-B4	Negative electrode B4	CNT dispersion B4	B	B
	Example 2-C1	Negative electrode C1	CNT dispersion C1	B	B
	Example 2-C2	Negative electrode C2	CNT dispersion C2	B	B
	Example 2-C3	Negative electrode C3	CNT dispersion C3	A	B
	Example 2-D1	Negative electrode D1	CNT dispersion D1	B	B
	Example 2-D2	Negative electrode D2	CNT dispersion D2	B	B

(continued)

	Negative electrode	Conductive material dispersion	Volume resistivity	Peel strength	
5	Example 2-D3	Negative electrode D3	CNT dispersion D3	B	B
10	Example 2-D4	Negative electrode D4	CNT dispersion D4	B	B
15	Example 2-E1	Negative electrode E1	CB dispersion E1	B	B
20	Example 2-E2	Negative electrode E2	CB dispersion E2	B	B
25	Example 2-E3	Negative electrode E3	CB dispersion E3	B	B
30	Comparative Example 2- a1	Negative electrode a1	CNT dispersion a1	D	B
35	Comparative Example 2- a2	Negative electrode a2	CNT dispersion a2	D	B
40	Comparative Example 2- a3	Negative electrode a3	CNT dispersion a3	D	B
45	Comparative Example 2- a4	Negative electrode a4	CNT dispersion a4	D	B
50	Comparative Example 2- a5	Negative electrode a5	CNT dispersion a5	D	B
55	Comparative Example 2- a6	Negative electrode a6	CNT dispersion a6	D	B
	Comparative Example 2- a7	Negative electrode a7	CNT dispersion a7	D	D
	Comparative Example 2- a8	Negative electrode a8	CNT dispersion a8	D	D
	Comparative Example 2- a9	Negative electrode a9	CNT dispersion a9	D	D
	Comparative Example 2- a10	Negative electrode a10	CNT dispersion a10	D	B
	Comparative Example 2- a11	Negative electrode a11	CNT dispersion a11	D	B
	Comparative Example 2- a12	Negative electrode a12	CNT dispersion a12	D	B
	Comparative Example 2- a13	Negative electrode a13	CNT dispersion a13	D	D
	Comparative Example 2- a14	Negative electrode a14	CNT dispersion a14	D	D
	Comparative Example 2- a15	Negative electrode a15	CNT dispersion a15	D	D
	Comparative Example 2- a16	Negative electrode a16	CB dispersion a1	D	B
	Comparative Example 2- a17	Negative electrode a17	CB dispersion a2	B	D
	Comparative Example 2- d1	Negative electrode d1	CNT dispersion b1	D	D
	Comparative Example 2- d2	Negative electrode d2	CNT dispersion b2	D	D
	Comparative Example 2- d3	Negative electrode d3	CNT dispersion b3	D	D

[0151] All of the negative electrodes using the conductive material dispersions of the above embodiments had good conductivity and adhesion. This may be due to the fact that the dispersing agent was able to act effectively by satisfying the structural requirements of the above embodiments. Furthermore, the carbon layer of the fine silicon-based active

material coated with carbon used in the examples has a surface state similar to that of the CNT in which the amount of acidic groups in the above embodiment is in a specific range, and the silicon-based active material has a surface which is negatively charged in water. From the above, the carbon layer has a particularly excellent interaction with the CNT dispersion, and the reason seems to be because a good material distribution state is formed even in the dried electrode film.

(Preparation of positive electrode mixture composition and positive electrode)

[0152] The abbreviations described in the following description are as follows.

- LFP: lithium iron phosphate HED (trademark) LFP-400 (manufactured by BASF, non-volatile content 100%)
- PTFE: polytetrafluoroethylene Polyflon PTFE D-210C (manufactured by DAIKIN INDUSTRIES, LTD., non-volatile content 60%)
- MAC500LC: carboxymethyl cellulose sodium salt, SUNROSE Special Type MAC500LC (manufactured by NIPPON PAPER INDUSTRIES CO., LTD., non-volatile content 100%)

(Example 3-A1)

[0153] A conductive material dispersion (a conductive material dispersion A1), MAC500LC, and water were added to a plastic container having a capacity of 150 cm³. Thereafter, the mixture was stirred at 2,000 rpm for 30 seconds by using a rotation/revolution mixer (Awa-tori Rentaro, ARE-310 manufactured by THINKY CORPORATION). Then, LFP was added as a positive electrode active material, and the mixture was stirred at 2,000 rpm for 150 seconds by using the rotation/revolution mixer (Awa-tori Rentaro, ARE-310 manufactured by THINKY CORPORATION). Thereafter, PTFE was added and the mixture was stirred at 2,000 rpm for 30 seconds by using the rotation/revolution mixer (Awa-tori Rentaro, ARE-310 manufactured by THINKY CORPORATION). Accordingly, a positive electrode mixture composition was obtained. The non-volatile content of the positive electrode mixture composition was 75 mass%. Among the non-volatile content of the positive electrode mixture composition, the ratio of LFP : conductive material : PTFE : non-volatile content of MAC500LC was 97:0.5:1:1.5.

[0154] The positive electrode mixture composition was coated on an aluminum foil having a thickness of 20 μm by using an applicator and then dried in an electric oven at 120 °C \pm 5 °C for 25 minutes to prepare an electrode film. Thereafter, the electrode film was rolled by means of a roll press (3t hydraulic roll press manufactured by THANK METAL CO., LTD) and accordingly a positive electrode (a positive electrode A1) was obtained. The weight per unit of the mixture layer was 20 mg/cm². The density of the mixture layer after performing the rolling treatment was 2.1 g/cc.

(Examples 3-A2 to 3-A25, 3-B1 to 3-B4, 3-C1 to 3-C3, 3-D1 to 3-D4, 3-E1 to 3-E3, and Comparative Examples 3-a1 to 3-a17, and 3-d1 to 3-d3)

[0155] Positive electrodes A2 to A25, positive electrodes B1 to B3, positive electrodes C1 to C3, positive electrodes D1 to D4, positive electrodes a1 to a17, and positive electrodes d1 to d3 were obtained by means of the same method as in Example 3-A1 except that the CNT dispersions were changed to the CNT dispersions shown in Table 6 (CNT dispersions A2 to A25, CNT dispersions B1 to B4, CNT dispersions C1 to C3, CNT dispersions D1 to D4, CB Dispersions E1 to E3, CNT dispersions a1 to a15, dispersions a1 and a2, and CNT dispersions d1 to d3).

(Method for evaluating conductivity of positive electrode)

[0156] Conductivity of the obtained positive electrode was evaluated by means of the same method as the negative electrode except that aluminum foil was used instead of copper foil.

Determination criteria

[0157]

- A: Less than 10 $\Omega\cdot\text{cm}$ (Excellent)
- B: 10 $\Omega\cdot\text{cm}$ or more and less than 20 $\Omega\cdot\text{cm}$ (Good)
- D: 20 $\Omega\cdot\text{cm}$ or more (Poor)

(Method for evaluating adhesion of positive electrode)

[0158] Adhesion of the obtained positive electrode was evaluated by means of the same method as the negative electrode except that aluminum foil was used instead of copper foil.

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Determination criteria

[0159]

10

- A: 1 N/cm or more (Excellent)
- B: 0.5 N/cm or more and less than 1 N/cm (Good)
- D: less than 0.5 N/cm (Poor)

15

[Table 6]

[0160]

Table 6

	Positive electrode	Conductive material dispersion	Volume resistivity	Peel strength	
20	Example 3-A1	Positive electrode A1	CNT dispersion A1	B	B
25	Example 3-A2	Positive electrode A2	CNT dispersion A2	B	B
30	Example 3-A3	Positive electrode A3	CNT dispersion A3	B	B
35	Example 3-A4	Positive electrode A4	CNT dispersion A4	B	B
40	Example 3-A5	Positive electrode A5	CNT dispersion A5	B	B
45	Example 3-A6	Positive electrode A6	CNT dispersion A6	A	A
50	Example 3-A7	Positive electrode A7	CNT dispersion A7	A	A
55	Example 3-A8	Positive electrode A8	CNT dispersion A8	A	A
	Example 3-A9	Positive electrode A9	CNT dispersion A9	B	B
	Example 3-A10	Positive electrode A10	CNT dispersion A10	A	B
	Example 3-A11	Positive electrode A11	CNT dispersion A11	B	B
	Example 3-A12	Positive electrode A12	CNT dispersion A12	B	B
	Example 3-A13	Positive electrode A13	CNT dispersion A13	A	B
	Example 3-A14	Positive electrode A14	CNT dispersion A14	A	B
	Example 3-A15	Positive electrode A15	CNT dispersion A15	A	B
	Example 3-A16	Positive electrode A16	CNT dispersion A16	A	A
	Example 3-A17	Positive electrode A17	CNT dispersion A17	A	B
	Example 3-A18	Positive electrode A18	CNT dispersion A18	A	B
	Example 3-A19	Positive electrode A19	CNT dispersion A19	A	A

(continued)

	Positive electrode	Conductive material dispersion	Volume resistivity	Peel strength	
5	Example 3-A20	Positive electrode A20	CNT dispersion A20	A	A
10	Example 3-A21	Positive electrode A21	CNT dispersion A21	A	A
15	Example 3-A22	Positive electrode A22	CNT dispersion A22	A	A
20	Example 3-A23	Positive electrode A23	CNT dispersion A23	A	A
25	Example 3-A24	Positive electrode A24	CNT dispersion A24	A	A
30	Example 3-A25	Positive electrode A25	CNT dispersion A25	A	A
35	Example 3-B1	Positive electrode B1	CNT dispersion B1	B	A
40	Example 3-B2	Positive electrode B2	CNT dispersion B2	A	A
45	Example 3-B3	Positive electrode B3	CNT dispersion B3	A	A
50	Example 3-B4	Positive electrode B4	CNT dispersion B4	B	B
55	Example 3-C1	Positive electrode C1	CNT dispersion C1	B	B
	Example 3-C2	Positive electrode C2	CNT dispersion C2	B	B
	Example 3-C3	Positive electrode C3	CNT dispersion C3	A	B
	Example 3-D1	Positive electrode D1	CNT dispersion D1	B	B
	Example 3-D2	Positive electrode D2	CNT dispersion D2	B	B
	Example 3-D3	Positive electrode D3	CNT dispersion D3	B	B
	Example 3-D4	Negative electrode D4	CNT dispersion D4	B	B
	Example 3-E1	Negative electrode E1	CB dispersion E1	B	B
	Example 3-E2	Negative electrode E2	CB dispersion E2	B	B
	Example 3-E3	Negative electrode E3	CB dispersion E3	B	B
	Comparative Example 3- a1	Positive electrode a1	CNT dispersion a1	D	D
	Comparative Example 3- a2	Positive electrode a2	CNT dispersion a2	D	D
	Comparative Example 3- a3	Positive electrode a3	CNT dispersion a3	D	D
	Comparative Example 3- a4	Positive electrode a4	CNT dispersion a4	D	D
	Comparative Example 3- as	Positive electrode as	CNT dispersion as	D	B
	Comparative Example 3- a6	Positive electrode a6	CNT dispersion a6	D	B
	Comparative Example 3- a7	Positive electrode a7	CNT dispersion a7	D	D
	Comparative Example 3- a8	Positive electrode a8	CNT dispersion a8	D	D
	Comparative Example 3- a9	Positive electrode a9	CNT dispersion a9	D	D

(continued)

	Positive electrode	Conductive material dispersion	Volume resistivity	Peel strength	
5	Comparative Example 3-a10	Positive electrode a10	CNT dispersion a10	D	D
10	Comparative Example 3-a11	Positive electrode a11	CNT dispersion a11	D	B
15	Comparative Example 3-a12	Positive electrode a12	CNT dispersion a12	D	B
20	Comparative Example 3-a13	Positive electrode a13	CNT dispersion a13	D	D
25	Comparative Example 3-a14	Positive electrode a14	CNT dispersion a14	D	D
30	Comparative Example 3-a15	Positive electrode a15	CNT dispersion a15	D	D
35	Comparative Example 3-a16	Positive electrode a16	CB dispersion a1	D	B
40	Comparative Example 3-a17	Positive electrode a17	CB dispersion a2	B	D
45	Comparative Example 3-d1	Positive electrode d1	CNT dispersion b1	D	D
50	Comparative Example 3-d2	Positive electrode d2	CNT dispersion b2	D	D
55	Comparative Example 3-d3	Positive electrode d3	CNT dispersion b3	D	D

[0161] All of the positive electrodes using the conductive material dispersions of the above embodiments had good conductivity and adhesion. This may be due to the fact that, as in the case of the negative electrode, the dispersing agent was able to act effectively by satisfying the structural requirements of the above embodiments. Further, as in the case of the silicon-based active material, the carbon layer of the fine lithium iron phosphate coated with carbon used in the examples has a surface state similar to that of the CNT in which the amount of acidic groups is in a specific range, and the lithium iron phosphate has a surface which is negatively charged in water. From the above, the carbon layer has a particularly excellent interaction with the CNT dispersion, and the reason seems to be because a good material distribution state is formed even in the dried electrode film.

(Preparation of standard positive electrode)

[0162] Amounts of 92 parts by mass of LFP (HED (trademark) LFP-400, manufactured by BASF, non-volatile content 100%), 4 parts by mass of acetylene black (Denka black (registered trademark) HS-100, manufactured by Denka Company Limited., non-volatile content 100%), and 1.6 parts by mass of MAC500LC (carboxymethyl cellulose sodium salt SUNROSE Special Type MAC500L, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., non-volatile content 100%) as positive electrode active materials were added to a plastic container having a capacity of 150 ml. Then the mixture was mixed by using a spatula until the powders became uniform. Thereafter, 25 parts by mass of water was added and the mixture was stirred at 2,000 rpm for 30 seconds by using a rotation/revolution mixer (Awa-ori Rentaro, ARE-310 manufactured by THINKY CORPORATION). Thereafter, the mixture in the plastic container was mixed by using the spatula until the mixture became uniform. An amount of 4 parts by mass of PTFE (manufactured by DAIKIN INDUSTRIES, LTD., non-volatile content 60 mass%) was added and the mixture was stirred at 2,000 rpm for 30 seconds by using the rotation/revolution mixer. Thereafter, 11.2 parts by mass of water was added, and the mixture was stirred at 2,000 rpm for 30 seconds by using the rotation/revolution mixer. Finally, the mixture was stirred at 3,000 rpm for 10 minutes by using a high-speed agitator. Accordingly, a standard positive electrode mixture composition was obtained. The non-volatile content of the standard positive electrode mixture composition was 79 mass%.

[0163] The above described standard positive electrode mixture composition was coated on an aluminum foil with a thickness of 20 μm serving as a current collector by using an applicator. Thereafter, the composition was dried at 120 $^{\circ}\text{C} \pm 5$ $^{\circ}\text{C}$ for 25 minutes in an electric oven and an adjustment was made such that the weight per unit area of the

electrode became 20 mg/cm². A rolling treatment was performed by using a roll press (3t hydraulic roll press manufactured by THANK METAL CO., LTD.) and accordingly a standard positive electrode in which a mixture layer density was 2.1 g/cm³ was prepared.

5 (Preparation of standard negative electrode)

[0164] Amounts of 0.5 parts by mass of acetylene black (Denka black (registered trademark) HS-100, manufactured by Denka Company Limited.), 1 part by mass of MAC500LC (carboxymethyl cellulose sodium salt SUNROSE Special Type MAC500L, manufactured by NIPPON PAPER INDUSTRIES CO., LTD., non-volatile content 100%), and 98.4 parts by mass of water were added to a plastic container having a capacity of 150 ml. Thereafter, the mixture was stirred at 2,000 rpm for 30 seconds by using a rotation/revolution mixer (Awa-tori Rentaro, ARE-310 manufactured by THINKY CORPORATION). Further, 87 parts by mass of artificial graphite (CGB-20, manufactured by Nippon Graphite Industries, Co., Ltd.) and 10 parts by mass of silicon were added to the mixture as active materials and the resultant mixture was stirred at 2,000 rpm for 150 seconds by using the rotation/revolution mixer (Awa-tori Rentaro, ARE-310 manufactured by THINKY CORPORATION). Subsequently, 3.1 parts by mass of SBR (TRD2001, manufactured by JSR CORPORATION) was added to the mixture and the resultant mixture was stirred at 2,000 rpm for 30 seconds by using the rotation/revolution mixer (Awa-tori Rentaro, ARE-310 manufactured by THINKY CORPORATION). Accordingly, a standard negative electrode mixture composition was obtained. The non-volatile content of the standard negative electrode mixture composition was 50 mass%.

[0165] The above described standard negative electrode mixture composition was coated on a copper foil with a thickness of 20 μ m serving as a current collector by using an applicator. Thereafter, the composition was dried at 80 °C \pm 5 °C for 25 minutes in an electric oven and an adjustment was made such that the weight per unit area of the electrode became 10 mg/cm². A rolling treatment was performed by using a roll press (3t hydraulic roll press manufactured by THANK METAL CO., LTD.), and accordingly a standard negative electrode in which a mixture layer density was 1.6 g/cm³ was prepared.

(Examples 4-A1 to 4-A25, 4-B1 to 4-B4, 4-C1 to 4-C3, 4-D1 to 4-D4, 4-E1 to 4-E3, and Comparative Examples 4-a1 to 4-a17 and 4-d1 to 4-d3)

30 (Examples 5-A1 to 5-A25, 5-B1 to 5-B4, 5-C1 to 5-C3, 5-D1 to 5-D4, 5-E1 to 5-E3, and Comparative Examples 5-a1 to 5-a17, and 5-d1 to 5-d3)

(Preparation of secondary battery)

35 [0166] The negative electrode and the positive electrode shown in Tables 7 and 8 were punched into 50 mm \times 45 mm and 45 mm \times 40 mm shapes, and a separator (a porous polypropylene film) inserted between the electrodes and the punched electrodes were inserted into an aluminum laminate bag. The electrodes and the separator were dried in an electric oven at 70 °C for 1 hour. Thereafter, 2 mL of electrolyte was injected into a glove box filled with argon gas. The electrolyte was nonaqueous electrolyte obtained by preparing a mixed solvent in which ethylene carbonate, dimethyl carbonate, and diethyl carbonate are mixed at a volume ratio of 1:1:1, adding 1 part by mass of vinylene carbonate as an additive relative to 100 parts by mass, and then dissolving LiPF₆ at a concentration of 1M. Then, the aluminum laminate was sealed and a secondary battery was prepared.

(Method for evaluating rate characteristic of secondary battery)

45 [0167] The obtained secondary battery was placed in a constant temperature chamber at 25 °C and charge/discharge measurement was performed by using a charge/discharge device (SM-8 manufactured by HOKUTO DENKO CORPORATION). Constant current/constant voltage charging (a cutoff current of 1 mA (0.02 C)) was performed at a charge termination voltage of 4.3 V and a charging current of 10 mA (0.2 C). Thereafter, constant current discharge was performed at a discharge termination voltage of 3 V and a discharging current of 10 mA (0.2 C). After repeating the above operation three times, constant current/constant voltage charging (a cutoff current (1 mA (0.02 C)) was performed at a charging current of 10 mA (0.2 C) and a charge termination voltage of 4.3 V and constant current discharge was performed at discharging currents of 0.2 C and 3 C until the discharge termination voltage reached 3.0 V. Accordingly, discharge capacities were obtained. The rate characteristic can be expressed by means of Mathematical Formula 1 below by using the ratio of the 0.2 C discharge capacity to the 3C discharge capacity.

(Mathematical Formula 1) Rate characteristic = 3 C discharge capacity / third 0.2 C discharge capacity $\times 100$ (%)

5 Determination criteria

[0168]

- 10 A: 80% or more (Excellent)
- B: 60% or more and less than 80% (Good)
- D: Less than 60% (Poor)

(Method for evaluating cycle characteristic of secondary battery)

15 [0169] The obtained secondary battery was placed in a constant temperature chamber at 25 °C and charge/discharge measurement was performed by using a charge/discharge device (SM-8 manufactured by HOKUTO DENKO CORPORATION). After performing constant current/constant voltage charging (a cutoff current of 2.5 mA (0.05 C)) at a charge termination voltage of 4.3 V and a charging current of 25 mA (0.5 C), constant current discharge was performed at a discharge termination voltage of 3 V and a discharging current of 25 mA (0.5 C). The above operation was repeated 200 times. The cycle characteristic can be expressed by means of Mathematical Formula 2 below by using the ratio of the third 0.5 C discharge capacity to the 200th 0.5 C discharge capacity at 25 °C.

(Mathematical Formula 2) Cycle characteristic = 3rd 0.5 C discharge capacity / 200th 0.5 C discharge capacity $\times 100$ (%)

25 Determination criteria

[0170]

- 30 A: 85% or more (Excellent)
- B: 80% or more and less than 85% (Good)
- D: Less than 80% (Poor)

35 [Table 7]

[0171]

Table 7

	Positive electrode	Negative electrode	Rate characteristic	Cycle characteristic
40 Example 4-A1	Standard positive electrode	Negative electrode A1	B	B
45 Example 4-A2	Standard positive electrode	Negative electrode A2	B	B
50 Example 4-A3	Standard positive electrode	Negative electrode A3	A	A
55 Example 4-A4	Standard positive electrode	Negative electrode A4	B	B
	Standard positive electrode	Negative electrode A5	A	B
	Standard positive electrode	Negative electrode A6	A	A

(continued)

	Positive electrode	Negative electrode	Rate characteristic	Cycle characteristic	
5	Example 4-A7	Standard positive electrode	Negative electrode A7	A	A
10	Example 4-A8	Standard positive electrode	Negative electrode A8	A	A
15	Example 4-A9	Standard positive electrode	Negative electrode A9	B	B
20	Example 4-A10	Standard positive electrode	Negative electrode A10	A	B
25	Example 4-A11	Standard positive electrode	Negative electrode A11	B	B
30	Example 4-A12	Standard positive electrode	Negative electrode A12	B	B
35	Example 4-A13	Standard positive electrode	Negative electrode A13	A	B
40	Example 4-A14	Standard positive electrode	Negative electrode A14	A	B
45	Example 4-A15	Standard positive electrode	Negative electrode A15	A	A
50	Example 4-A16	Standard positive electrode	Negative electrode A16	A	A
55	Example 4-A17	Standard positive electrode	Negative electrode A17	A	B
	Example 4-A18	Standard positive electrode	Negative electrode A18	A	B
	Example 4-A19	Standard positive electrode	Negative electrode A19	A	A
	Example 4-A20	Standard positive electrode	Negative electrode A20	A	A
	Example 4-A21	Standard positive electrode	Negative electrode A21	A	A
	Example 4-A22	Standard positive electrode	Negative electrode A22	A	A
	Example 4-A23	Standard positive electrode	Negative electrode A23	A	A
	Example 4-A24	Standard positive electrode	Negative electrode A24	A	A
	Example 4-A25	Standard positive electrode	Negative electrode A25	A	A
	Example 4-B1	Standard positive electrode	Negative electrode B1	B	A
	Example 4-B2	Standard positive electrode	Negative electrode B2	A	A
	Example 4-B3	Standard positive electrode	Negative electrode B3	A	B

(continued)

	Positive electrode	Negative electrode	Rate characteristic	Cycle characteristic	
5	Example 4-B4	Standard positive electrode	Negative electrode B4	B	B
10	Example 4-C1	Standard positive electrode	Negative electrode C1	B	B
15	Example 4-C2	Standard positive electrode	Negative electrode C2	B	B
20	Example 4-C3	Standard positive electrode	Negative electrode C3	A	A
25	Example 4-D1	Standard positive electrode	Negative electrode D1	B	B
30	Example 4-D2	Standard positive electrode	Negative electrode D2	B	B
35	Example 4-D3	Standard positive electrode	Negative electrode D3	B	B
40	Example 4-D4	Standard positive electrode	Negative electrode D4	B	B
45	Example 4-E1	Standard positive electrode	Negative electrode E1	B	B
50	Example 4-E2	Standard positive electrode	Negative electrode E2	B	B
55	Example 4-E3	Standard positive electrode	Negative electrode E3	B	B
	Comparative Example 4- a1	Standard positive electrode	Negative electrode a1	D	D
	Comparative Example 4- a2	Standard positive electrode	Negative electrode a2	D	D
	Comparative Example 4- a3	Standard positive electrode	Negative electrode a3	D	D
	Comparative Example 4- a4	Standard positive electrode	Negative electrode a4	D	D
	Comparative Example 4- a5	Standard positive electrode	Negative electrode a5	D	D
	Comparative Example 4- a6	Standard positive electrode	Negative electrode a6	D	D
	Comparative Example 4- a7	Standard positive electrode	Negative electrode a7	D	D
	Comparative Example 4- a8	Standard positive electrode	Negative electrode a8	D	D
	Comparative Example 4- a9	Standard positive electrode	Negative electrode a9	D	D
	Comparative Example 4- a10	Standard positive electrode	Negative electrode a10	D	D
	Comparative Example 4- a11	Standard positive electrode	Negative electrode a11	D	D

(continued)

	Positive electrode	Negative electrode	Rate characteristic	Cycle characteristic	
5	Comparative Example 4- a12	Standard positive electrode	Negative electrode a12	D	D
10	Comparative Example 4- a13	Standard positive electrode	Negative electrode a13	D	D
15	Comparative Example 4- a14	Standard positive electrode	Negative electrode a14	D	D
20	Comparative Example 4- a15	Standard positive electrode	Negative electrode a15	D	D
25	Comparative Example 4- a16	Standard positive electrode	Negative electrode a16	D	D
	Comparative Example 4- a17	Standard positive electrode	Negative electrode a17	D	D
30	Comparative Example 4- d1	Standard positive electrode	Negative electrode d1	D	D
35	Comparative Examole 4- d2	Standard positive electrode	Negative electrode d2	D	D
40	Comparative Examole 4- d3	Standard positive electrode	Negative electrode d3	D	D

[Table 8]

[0172]

Table 8

	Positive electrode	Negative electrode	Rate characteristic	Cycle characteristic	
35	Example 5-A1	Positive electrode A1	Standard negative electrode	B	B
40	Example 5-A2	Positive electrode A2	Standard negative electrode	A	B
45	Example 5-A3	Positive electrode A3	Standard negative electrode	A	B
50	Example 5-A4	Positive electrode A4	Standard negative electrode	B	B
55	Example 5-A5	Positive electrode A5	Standard negative electrode	A	B
	Example 5-A6	Positive electrode A6	Standard negative electrode	A	B
	Example 5-A7	Positive electrode A7	Standard negative electrode	A	B
	Example 5-A8	Positive electrode A8	Standard negative electrode	A	B
	Example 5-A9	Positive electrode A9	Standard negative electrode	B	B

(continued)

	Positive electrode	Negative electrode	Rate characteristic	Cycle characteristic
5	Example 5-A10	Positive electrode A10	Standard negative electrode	A B
10	Example 5-A 11	Positive electrode A11	Standard negative electrode	B B
15	Example 5-A12	Positive electrode A12	Standard negative electrode	B B
20	Example 5-A13	Positive electrode A13	Standard negative electrode	A B
25	Example 5-A14	Positive electrode A14	Standard negative electrode	A B
30	Example 5-A15	Positive electrode A15	Standard negative electrode	A B
35	Example 5-A16	Positive electrode A16	Standard negative electrode	A B
40	Example 5-A17	Positive electrode A17	Standard negative electrode	A B
45	Example 5-A18	Positive electrode A18	Standard negative electrode	A B
50	Example 5-A19	Positive electrode A19	Standard negative electrode	A B
55	Example 5-A20	Positive electrode A20	Standard negative electrode	A B
	Example 5-A21	Positive electrode A21	Standard negative electrode	A B
	Example 5-A22	Positive electrode A22	Standard negative electrode	A B
	Example 5-A23	Positive electrode A23	Standard negative electrode	A B
	Example 5-A24	Positive electrode A24	Standard negative electrode	A B
	Example 5-A25	Positive electrode A25	Standard negative electrode	A B
	Example 5-B1	Positive electrode B1	Standard negative electrode	B B
	Example 5-B2	Positive electrode B2	Standard negative electrode	A B
	Example 5-B3	Positive electrode B3	Standard negative electrode	A B
	Example 5-B4	Positive electrode B4	Standard negative electrode	B B
	Example 5-C1	Positive electrode C1	Standard negative electrode	B B
	Example 5-C2	Positive electrode C2	Standard negative electrode	B B

(continued)

	Positive electrode	Negative electrode	Rate characteristic	Cycle characteristic	
5	Example 5-C3	Positive electrode C3	Standard negative electrode	A	B
10	Example 5-D1	Positive electrode D1	Standard negative electrode	B	B
15	Example 5-D2	Positive electrode D2	Standard negative electrode	B	B
20	Example 5-D3	Positive electrode D3	Standard negative electrode	B	B
25	Example 5-D4	Positive electrode D4	Standard negative electrode	B	B
30	Example 5-E1	Positive electrode E1	Standard negative electrode	B	B
35	Example 5-E2	Positive electrode E2	Standard negative electrode	B	B
40	Example 5-E3	Positive electrode E3	Standard negative electrode	B	B
45	Comparative Example 5-a1	Positive electrode a1	Standard negative electrode	D	B
50	Comparative Example 5-a2	Positive electrode a2	Standard negative electrode	D	B
55	Comparative Example 5-a3	Positive electrode a3	Standard negative electrode	D	B
	Comparative Example 5-a4	Positive electrode a4	Standard negative electrode	D	B
	Comparative Example 5-a5	Positive electrode a5	Standard negative electrode	D	B
	Comparative Example 5-a6	Positive electrode a6	Standard negative electrode	D	B
	Comparative Example 5-a7	Positive electrode a7	Standard negative electrode	D	B
	Comparative Example 5-a8	Positive electrode a8	Standard negative electrode	D	B
	Comparative Example 5-a9	Positive electrode a9	Standard negative electrode	D	B
	Comparative Example 5-a10	Positive electrode a10	Standard negative electrode	D	B
	Comparative Example 5-a11	Positive electrode a11	Standard negative electrode	D	B
	Comparative Example 5-a12	Positive electrode a12	Standard negative electrode	D	B
	Comparative Example 5-a13	Positive electrode a13	Standard negative electrode	D	B
	Comparative Example 5-a14	Positive electrode a14	Standard negative electrode	D	B

(continued)

	Positive electrode	Negative electrode	Rate characteristic	Cycle characteristic	
5	Comparative Example 5-a15	Positive electrode a15	Standard negative electrode	D	B
10	Comparative Example 5-a16	Positive electrode a16	Standard negative electrode	D	B
15	Comparative Example 5-a17	Positive electrode a17	Standard negative electrode	D	B
20	Comparative Example 5-d1	Positive electrode d1	Standard negative electrode	D	B
25	Comparative Example 5-d2	Positive electrode d2	Standard negative electrode	D	B
	Comparative Example 5-d3	Positive electrode d3	Standard negative electrode	D	B

[0173] In the above examples using the conductive material dispersions of the above embodiments, a nonaqueous electrolyte secondary battery having more excellent cycle characteristics than that in the comparative examples was obtained. Therefore, it has become clear that the above described embodiments can provide a nonaqueous electrolyte secondary battery having cycle characteristics which are difficult to realize if a conventional conductive material dispersion is used.

Claims

30 1. A conductive material dispersion comprising:

a conductive material containing at least one kind selected from the group consisting of a carbon nanotube and carbon black;
 carboxymethyl cellulose or its salt; and
 35 water, wherein
 the carboxymethyl cellulose or its salt has a weight average molecular weight of 10,000 to 150,000 and an etherification degree of 0.5 to 0.9, and
 a product of a complex elastic modulus (Pa) and a phase angle (°) of the conductive material dispersion is 100 or more and 1,500 or less.

40 2. The conductive material dispersion according to claim 1, wherein

the carboxymethyl cellulose or its salt has a weight average molecular weight of 10,000 to 100,000.

45 3. A conductive material dispersion comprising:

a carbon nanotube;
 carboxymethyl cellulose or its salt; and
 water, wherein
 the carboxymethyl cellulose or its salt has a weight average molecular weight of 10,000 to 100,000 and an etherification degree of 0.5 to 0.9, and
 50 a product of a complex elastic modulus (Pa) and a phase angle (°) of the conductive material dispersion is 100 or more and 1,500 or less.

55 4. The conductive material dispersion according to claim 3, wherein

an amount of an acidic group of the carbon nanotube is 0.1 to 0.8 $\mu\text{mol}/\text{m}^2$.

5. The conductive material dispersion according to claim 3 or 4, wherein

an amount of an acidic group of the carbon nanotube is 40 to 500 $\mu\text{mol}/\text{g}$.

6. The conductive material dispersion according to any one of claim 1 and claims 3 to 5, wherein
the complex elastic modulus is 50 Pa or less and the phase angle is 15 degrees or more.

7. The conductive material dispersion according to any one of claims 3 to 6, wherein

5 the carbon nanotube includes a first carbon nanotube having an average outer diameter of 0.5 nm or more and
less than 5 nm and a second carbon nanotube having an average outer diameter of 5 nm or more and 20 nm
or less, and
a mass ratio of the first carbon nanotube to the second carbon nanotube is 1:10 to 1:100.

10 8. The conductive material dispersion according to any one of claims 3 to 7, further comprising:
a polyacrylic acid.

15 9. The conductive material dispersion according to any one of claim 1 and claims 3 to 8, wherein
a median diameter of the conductive material dispersion is 0.5 μm or more and 2.0 μm or less.

10. The conductive material dispersion according to any one of claim 1 and claims 3 to 9, wherein
the conductive material dispersion has a TI value of 2.0 to 5.0.

20 11. The conductive material dispersion according to any one of claim 1 and claims 3 to 10, wherein
a gloss of a coating film of the conductive material dispersion, measured at 60 degrees relative to an angle of
incidence, is 5 to 120.

25 12. The conductive material dispersion according to any one of claim 1 and claims 3 to 11, wherein
the conductive material dispersion has a pH of 7.0 to 10.5.

13. A composition for a secondary battery electrode comprising:
the conductive material dispersion according to any one of claims 1 to 12.

30 14. An electrode film comprising:
a coating film of the composition for a secondary battery electrode according to claim 13.

15. A secondary battery comprising:
the electrode film according to claim 14.

35 16. A method for producing the conductive material dispersion according to any one of claims 3 to 12 in which steps of
(1) and (2) below are performed in this order, the method comprising:

40 (1) a step of performing dispersing at a pressure of 60 to 120 MPa by using a high-pressure homogenizer and
setting a median diameter to 4.0 μm or less; and
(2) a step of performing dispersing until a phase angle becomes 40 degrees or more by using a bead mill.

17. A vehicle comprising:
the secondary battery according to claim 15.

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INTERNATIONAL SEARCH REPORT		International application No. PCT/JP2021/015040	
5	A. CLASSIFICATION OF SUBJECT MATTER H01M 4/04 (2006.01)i; H01M 4/13 (2010.01)i; H01M 4/139 (2010.01)i; H01M 4/62 (2006.01)i; C01B 32/174 (2017.01)i FI: H01M4/62 Z; H01M4/04 A; H01M4/139; H01M4/13; C01B32/174 According to International Patent Classification (IPC) or to both national classification and IPC		
10	B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) H01M4/04; H01M4/13; H01M4/139; H01M4/62; C01B32/174		
15	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2021 Registered utility model specifications of Japan 1996-2021 Published registered utility model applications of Japan 1994-2021		
20	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) JSTplus (JDreamIII)		
25	C. DOCUMENTS CONSIDERED TO BE RELEVANT		
30	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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40	A	JP 2018-534731 A (LG CHEM, LTD.) 22 November 2018 (2018-11-22) paragraphs [0170]-[0180]	1-17
45	A	JP 2020-001960 A (TOYO INK SC HOLDINGS CO., LTD.) 09 January 2020 (2020-01-09) paragraph [0126]	1-17
50	A	JP 2019-210173 A (TOYO INK SC HOLDINGS CO., LTD.) 12 December 2019 (2019-12-12) paragraph [0119]	1-17
55	E, X	JP 6860740 B1 (TOYO INK SC HOLDINGS CO., LTD.) 21 April 2021 (2021-04-21) claims 1-14	1-17
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.		<input checked="" type="checkbox"/> See patent family annex.	
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed			
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art		"&" document member of the same patent family	
50	Date of the actual completion of the international search 09 June 2021 (09.06.2021)		Date of mailing of the international search report 22 June 2021 (22.06.2021)
55	Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan		Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2021/015040

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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	Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
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30	JP 6860740 B1	21 Apr. 2021	(Family: none)	
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55	Form PCT/ISA/210 (patent family annex) (January 2015)			

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